RESULTS OF COMPARATIVE STUDIES OF PRESERVATION TECHNIQUES FOR NUTRIENT ANALYSIS ON WATER SAMPLES

A Report

To

The Environmental Protection Agency
Chesapeake Bay Liaison Office
410 Severn Avenue
Annapolis, Maryland 21403

by

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INTRODUCTION

Two generally accepted methods to handle water samples for nutrient analyses which also have been approved by the U.S. Environmental Protection Agency are: (1) to analyse the samples within 24 hours, or if this is not possible, (2) to analyse the samples within EPA recommended holding times. In addition, the holding times for some nutrient analyses can be extended by the addition of preservatives. Personnel constraints often preclude immediate analyses, but the addition of foreign substances (preservatives) can introduce contamination and cause other problems. The purpose of this study was to assess a third method, freezing, as a sample preservation alternative.

In this study, five different treatments (including two freezing treatments) were investigated. Four water samples were analysed for nine water quality constituents:

Orthophosphate	(OP)
Total dissolved phosphorus	(TDP)
Total phosphorus	(TP)
Nitrite	(NO2)
Nitrate-Nitrite	(NO23)
Ammonia	(NH3)
Total Kjeldahl Nitrogen	(TKN)
Silica	(Si)
Suspended solids	(SS)

Sampling

Sampling was done on April 30, 1986. Four stations (two on the James River and two on the York River) were sampled in order to give a diverse salinity range. The James River stations were 31.85 (James 1) and 50.19 (James 2) kilometers upstream from the river mouth and the York River stations were at 0.00 (York 1) and 19.21 (York 2) kilometers from the Bay. The Chesapeake Bay Program designations for these stations are LE5.2, LE5.1, WE4.2 and LE4.2, respectively. All

four stations have been monitored for a number of years. All samples were collected within an hour of each other and the samples were back in the laboratory within two hours of the last sample taken. Five carboys of water were collected at each station. Each sample was taken with a submersible pump at a depth of ten feet.

Sample processing

Concentrations for certain nutrients, particularly at the York River stations, were low; therefore, the samples were spiked in order that concentrations be above the lowest standard used for those analyses. The carboys for each station were poured into a large vat with a valve at the bottom, the additional nutrients were added (see Table 1), and the combined sample stirred with a paddle while aliquots were taken off. A carboy of each sample was withdrawn and given to personnel of the Maryland Office of Environmental Protection to process for particulate analyses.

Table 1. Approximate spike values (in mg/l) for each station.

STATION	NO2	NH3	OP
JAMES 1	0.005	----	----
JAMES 2	0.005	----	----
YORK 1	0.005	0.010	0.020
YORK 2	0.050	0.100	0.100

It was known from historical data that the concentrations of dissolved nutrients at the York River stations would be low. Except for the NO2 concentrations, the James River stations have had values above the lowest standards used in the analyses. Unfortunately, concentrations at the James stations were lower than in previous years, particularly in NH3, and concentrations were less than 0.010 mg/l, the lowest standard. The OP for the station York 1 also was below the lowest standard of 0.010 mg/l. The values for these analyses for these stations are in the data files, but the numbers are lower than generally reported. The mean concentrations for the four stations and nine constituents are shown in Table 2. The salinity

range was not as large as planned. The severe drought resulted in the salt water intrusion being further upriver than usual.

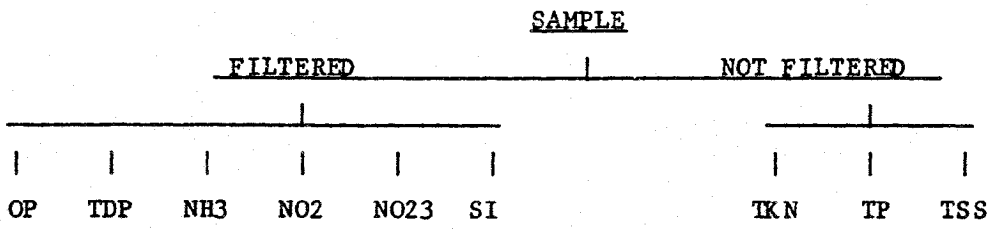
Table 2. Mean concentration of samples (in mg/l) after spiking Salinity concentration is in ppt.

ANALYSES	STATIONS			
	JAMES 1	JAMES 2	YORK 1	YORK 2
SALINITY	13.5	6.4	18.5	17.7
NO2	0.010	0.007	0.010	0.055
NO23	0.180	0.270	0.110	0.080
NH3	0.002	0.002	0.013	0.080
TKN	0.365	0.445	0.470	0.550
SI	0.660	1.270	0.035	0.065
TP	0.065	0.110	0.030	0.135
TDP	0.020	0.025	0.015	0.090
OP	0.010	0.015	0.005	0.080
TSS	16	38	7	20

The handling of the samples when they arrived in the laboratory was pre-orchestrated. First, samples for all the treatments and for all the analyses were to be processed and stored. In addition, the zero day samples were to be analysed as well. Given the intense work load on the first day there was a strong possibility for mishandling. This did occur with one sample for one treatment for two constituents. The sample for holding time from the York 2 station for NH3 and NO23 did not have H2SO4 added for preservation. This was not discovered until the time came to run the analyses and the pH was to be adjusted. There was also the odd replicate lost and this is indicated in the data files with '-.---'. Some of the replicate values were suspect and in normal sample handling, these samples would have been rerun. For this study, the values were kept in the data file because there was no attempt to identify and remove outliers.

As previously mentioned, a carboy of each sample was provided to the personnel from Maryland's Office of Evironmental Protection for processing for particulate analyses. The Virginia Institute of Marine Science portions were processed according to Table 3. In addition to samples for analysis in the Nutrient Analysis Lab, samples for TOC/DOC analyses were provided to Old Dominion University.

Table 3. Processing schema for the Nutrient Analysis Lab.



Sample Treatments

Each water quality constituent analysed received five treatments. First, samples were analysed on the day they were taken (Day 0) in order to have a reference ("true") value to which to compare the other treatments. Second, the samples were analysed the following day (Day 1). This was in accordance with our normal laboratory treatment of samples. Third, the samples were held for the EPA recommended time span with any necessary preservation (HT). Any storage time in the previous treatments was done at 4 degrees centigrade. The fourth and fifth treatments were conducted to test the effect of freezing on the samples. The samples were frozen at -20 degrees centigrade and, after seven days for the fourth treatment, thawed at room temperature (25 degrees centigrade) and then analysed. The fifth treatment was the same except the samples remained in the freezer for 28 days (FB). These treatments are summarized in Table 4. It was predetermined that thawing would take approximately 12 hours. The samples to be run were removed from the freezer the evening before analysis. In accordance with findings by MacDonald and McLaughlin (1982) that reactive silicate concentration is a function of thaw time for low salinity samples that have been filtered, silica samples were given an additional 12 hours after thawing to counter any freezing effect and the bottles were shaken particularly well before being analysed.

Table 4. Treatments investigated on each of the five days when samples were analysed.

ANALYSES \ DAY	0	1	2	7	28
NO2	X	N	HT	FA	FB
NO23	X	N		FA	HT*/FB
NH3	X	N		FA	HT*/FB
TKN	X	N		FA	HT*/FB
SI	X	N		FA	HT/FB
TP	X	N		FA	HT*/FB
TDP	X	N		FA	HT*/FB
OP	X	N	HT	FA	FB
TSS	X	N		HT/FA	FB

Treatments:
- X "TRUE VALUE" - Immediate analysis
- N NORMAL PROCESSING TIME
- HT EPA HOLDING TIME (* PH'ED TO 2N WITH H2SO4)
- FA 7 DAYS FROZEN
- FB 28 DAYS FROZEN

METHODS

Analytical Techniques

Ammonia, nitrite, nitrate-nitrite, and silica were analysed using the Technicon Autoanalyzer II according to Technicon methodology. Orthophosphate, total dissolved phosphorus, total phosphorus, total Kjeldahl nitrogen, and suspended solids were determined manually using EPA's, "Methods for Chemical Analysis of Water and Wastes".

Statistical Methods

Statistical techniques were employed to test whether the different treatments (i.e. laboratory analysis at Day 0, Day 1, after an analysis-specific holding time, at 7 days after freezing, and at 28 days after freezing) produced different results. Each water quality constituent (i.e. nitrite, nitrate-nitrite, ammonia, total Kjeldahl nitrogen, orthophosphate, total phosphorus, total dissolved phosphorus, silica, and suspended solids) was tested individually, as was each sampling station. In addition to hand calculations, the computer-based statistical packages SPSS (Nie, 1975) and SPSSX (SPSS Inc., 1986) were used for statistical analyses. In general, the null hypotheses tested by statistical procedures stated that the treatments produced equal results and were tested at alpha=0.05. Tables of results show the probability of getting test statistics at least as large as those calculated if the null hypothesis was indeed true. The null hypothesis was typically rejected when this probability fell below the chosen alpha level. When the probability was greater than the alpha level, the null hypothesis was accepted, and equality of treatments was concluded.

A series of paired t-tests was used to test differences between the control (Day 0) and each other treatment. Specifically, the null hypothesis stated that the mean difference between the control group (Day 0) and each other treatment was zero. Results of the paired t-tests are shown in Appendix C, Table C1.

The paired t-test was thought to be an appropriate test because of the relatedness of samples: within each station, each sample analyzed was originally split from one large sample rather than originating as an independent sample. However, in order to determine whether the control population is different from the treatment to which it is compared, the paired t-test calculates the difference between observed values for each case and determines whether the mean of these differences is significantly different from zero. For this study, the replicates were the cases to be considered, but replicate number 1 of the control group (Day 0) was not actually any more related to replicate 1 of the Day 1 group than it was to replicate 2 or 3, and so on, of the Day 1 group. Therefore, the pairings used for calculation of differences between treatments seem rather artificial and the meaningfulness of the results of the paired t-test is questionable. In addition, the stated null hypothesis suggests that the use of a multisample technique such as analysis of variance would be more appropriate than multiple use of the t-test, a two-sample technique.

One-way analysis of variance was used to test the hypothesis that the population means for each treatment, including Day 0, were equal. Two-way analysis of variance, with sampling station as the second factor, was determined inappropriate for two reasons: artificial variation between stations was produced when samples from some stations were spiked prior to analysis and other samples were not, and testing of the station effect was not relevant to the study objectives. Results of the one-way analysis of variance are shown in Table C2.

Once a significant difference between treatment means was established with analysis of variance, multiple comparisons procedures were employed to determine which treatments were different.

Dunnett's multiple comparisons procedure (Zar, 1984) was used to compare the control (Day 0) mean to each other treatment mean, testing the hypothesis that the control mean did not differ significantly from the other treatment means. Results of this procedure at alpha=0.05 and alpha=0.01 are shown in Table C3.

A second multiple comparisons procedure which seemed useful was Scheffe's multiple contrasts procedure, which compared the average of the means of the currently acceptable treatments (Day 0, Day 1, and Holding Time) with each of the freezing treatments. Specifically, the null hypothesis that was tested stated that the mean of the accepted treatment means (the composite control) was equal to the mean of the chosen freezing treatment. Results of this procedure are shown in Table C4.

It was also thought to be of interest not only to investigate differences between the control and other treatments, but also to investigate differences between all treatments. This was accomplished with Tukey's multiple comparisons procedure, testing the hypothesis that for each comparison, the two means compared were equal. Results are shown in Table C5.

The parametric analysis of variance and multiple comparisons techniques utilized assume that data are normally distributed and that treatment variances are equal. These assumptions appear to have been violated for some data groups in this study, as shown by the Kolmogorov-Smirnov test of normality (Table C6) and Bartlett's test of homogeneity of variances (Table C7). Although analysis of variance and the multiple comparisons procedures are thought to be rather robust to departures from the assumptions, nonparametric analysis of variance and multiple comparisons, which test means of value rankings rather than means of the values themselves, have also been included. The rank means used for nonparametric tests are shown in Table C8. Results of the Kruskal-Wallis nonparametric analysis of variance, testing the hypothesis that all treatments are equal, are shown in Table C9. Results of Dunn's nonparametric multiple comparisons technique, comparing all combinations of treatments to determine where differences exist, are shown in Table C10.

It is realized that computing multiple statistics from the same data can be considered poor technique. However, statisticians do not always agree on which statistics are appropriate for a given situation. Therefore, several statistics are provided so that the reader may choose the test deemed appropriate.

RESULTS

General

Appendix A contains raw data arranged by water quality constituent and includes means, standard deviations, minima, and maxima for each station (Tables A1 through A9).

Appendix B contains figures summarizing the results of the study. Figures B1 through B9 (one figure per water quality constituent) are plots of mean concentration vs. treatment, with each station's results shown as a separate line on each graph. These figures show the greater magnitude of differences between stations relative to differences between treatments.

In Figures B10 through B45, the mean concentrations vs. treatments for each of the stations are plotted on separate graphs, and standard deviations from the mean concentrations are added to the graphs to show the variability within each data group. The treatments were arranged on the X-axis to illustrate how the EPA-approved treatments (Day 0, Day 1, and Holding Time) compared with each other as well as how the freezing treatments compared with the "control" (Day 0). The control is situated in the middle of the X-axis, with Day 1 and Holding Time treatments running to the left, and Day 7(frozen) and Day 28(frozen) treatments running to the right. In theory, the variation in constituent concentrations described by the left half of the graphs is acceptable to EPA. For the freezing treatments (the right half of the graphs) to be accepted as being equivalent to the currently accepted treatments, they should fall within the range of variability described by the left half of the graph. This appeared to be the case for most of the analyses, with exception of silica and possibly some of the nitrate-nitrite, orthophosphate, and total phosphorus results.

The results will be described by water quality constituent. Results of the first analysis (nitrite) will be described in detail, and the remaining results will be described more generally. Results of statistical analyses for each constituent are summarized in

tables at the end of this section. Results of statistical procedures are also organized by statistical analysis in Appendix C.

Nitrite

Nitrite concentrations were generally higher at Day 0 than at any other time, fell at Day 1 and fell again at the Holding Time (Figures B10 through B13). The data from frozen samples seemed to generally fall within the range defined by data from the approved treatments (Day 0, Day 1, Holding Time), and variability of the frozen data did not appear to be greater than variability of the approved treatments.

Results of statistical analyses are shown in Table 5. The paired t-test showed significant differences between the control (Day 0) and all other treatments except Day 1 at stations James 1 and York 1. For reasons mentioned in the Statistical Methods section, the t-test results should be viewed with caution.

The parametric ANOVA results showed that all treatment means could not be considered equal for any of the sampling stations. Using Dunnett's multiple comparisons then to determine where differences existed between the control (Day 0) and the other treatments, significant differences were found between the control mean and all other treatment means, except for Day 1 at stations James 1 and York 1. Although the differences between means were statistically significant, examination of the treatment means showed that the actual difference between means in many cases was less than 0.001 mg/l, which was the smallest difference detectable by the equipment used for this study. Many of the statistically significant differences were therefore not practically significant. It is interesting to note that the treatment most different from the control was consistently the Holding Time treatment. In all cases, the frozen samples were more similar to the control than the Holding Time samples.

Scheffe's multiple contrasts procedure showed statistically significant differences between the mean of the means of accepted treatments (Day 0, Day 1 and Holding Time) and all freezing sample means except the Day 28(frozen) sample at James 2 and York 1. But these differences were in all cases, except the York 2 Day 7(frozen)

sample, smaller than the smallest difference detectable by the laboratory equipment used, and were therefore not measurably different.

Tukey's multiple comparisons also showed many significant differences between treatment means. Means that were not significantly different included Day 0 and Day 1 at stations James 1 and York 1, the two frozen samples at James 1 and York 1, Holding Time and the 7 day frozen sample at James 2, and the 28 day frozen sample and Day 1 at James 2. Again, however, these differences were often smaller than the smallest difference detectable with available analysis equipment.

The Kolmogorov-Smirnov test for normal distribution indicated that within each treatment at each station, the nitrite data were not normally distributed, so it may be prudent to examine the results of the nonparametric techniques. The Kruskal-Wallis nonparametric ANOVA indicated that the treatments were not all equal at any of the stations. Dunn's nonparametric multiple comparisons showed fewer significant differences between treatments than Tukey's multiple comparisons, with additional similarities including Day 0 and the 28 day frozen sample at all stations except James 1, Holding Time and the 7 day frozen sample at all stations, Day 0 and Day 1 at all stations, and the 28 day frozen sample with various combinations of the other treatments at different stations.

Nitrate-nitrite

An examination of Figures B14 through B17 showed that in general, Holding Time and Day 28(frozen) data seemed to be more variable than data for the other treatments. Nitrate-nitrite concentrations in the frozen samples tended to be slightly lower than the range defined by the approved treatments.

Results of statistical analyses are shown in Table 6. For nitrate-nitrite the frozen samples were not generally similar to the control. At James 1, Day 28(frozen) was different from all other treatments. At York 2, however, Day 0 was different from all other treatments. At York 1, Day 28(frozen) was different from all treatments except Day 7(frozen). At James 2, Day 7(frozen) was different

from Day 0 and Holding Time. Unlike the nitrite data, all statistically significant differences between treatment means were also measurable differences.

Although the nitrate-nitrite data appeared to be normally distributed, the variances of the treatment means were not equal, so use of the nonparametric statistics may be desired. These results were very similar to the parametric statistics results.

Ammonia

Figures B18 through B21 show that except at York 2, ammonia concentrations in the frozen samples generally fell within the range defined by the approved treatments. Holding Time data appeared to be more variable than other treatment data.

Results of statistical analyses are shown in Table 7. None of the statistical methods found any differences between any treatments at the James stations.

At York 1, the primary differences seemed to exist between Day 1 and the other treatments. At York 2, Day 28(frozen) was the only treatment different from the other treatments.

Total Kjeldahl Nitrogen

Total Kjeldahl nitrogen concentrations seemed to be more variable than other constituent concentrations. Except at James 1, the frozen sample data seemed to fall within the range defined by the data from approved treatments (Figures B22-B25). Compared to other treatments, Day 28(frozen) and Holding Time were generally less variable.

Results of statistical analyses are shown in Table 8. In general, all treatments were shown to be equal at James 2 and the two York stations. At James 1, the control (Day 0) was similar only to Day 28(frozen), while the composite control (Day 0, Day 1, Holding Time) was similar to both freezing treatments. Comparisons of other treatments found Day 28(frozen) to be different from Day 7(frozen) and Holding Time.

Orthophosphate

Frozen sample data did not consistently fall within the range defined by the data from approved treatments; at James 1 frozen orthophosphate concentrations were higher and at York 2 frozen orthophosphate concentrations were lower (Figures B26-B29).

Results of statistical analyses are shown in Table 9. The statistical methods showed many differences between treatments. However, as with the nitrite results, many of the differences between treatment means, although statistically significant, were not measurably different with the available lab equipment. This lack of measurable difference between means occurred at James 1 (where the smallest mean, Day 1, was 0.0105 mg/l, and the largest mean, Day 28(frozen), was 0.0115 mg/l) and York 1 (Day 1 mean, 0.0042 mg/l; holding time mean, 0.0052 mg/l). In addition, the only treatment mean measurably different from the control (Day 0) at James 2 was the Holding Time treatment. Scheffe's contrasts showed that Day 28(frozen) was statistically significantly different from the composite control at the James stations and York 2. However, the actual difference at James 1 was not measurable.

Total Dissolved Phosphorus

Frozen concentrations did not quite fall within the range defined by concentrations from approved treatments (Figures B30-B33). At York 2, total dissolved phosphorus concentrations were higher than at other stations, and differences between treatments seemed more evident than at other stations.

Results of statistical analyses are shown in Table 10. In general, the different treatments did not produce significantly different results at the James stations or York 1. At York 2, however, all treatments except Day 1 were different from the control and different from each other. The composite control was different only from Day 28(frozen).

The James stations and York 1 data were not normally distributed; York 2 data were normally distributed and had equal variances. It might be wise to use the nonparametric tests in the case of the James stations and York 1. Those tests showed differences

between Day 1 and other treatments at James 2, between Holding Time and other treatments at York 1. No differences existed between the control and the freezing treatments for nonparametric comparisons.

Total Phosphorus

Examination of Figures B34-B37 revealed that total phosphorus concentrations from frozen samples did not fall completely within the range defined by the approved treatments.

Results of statistical analyses are shown in Table 11. The different treatments seemed to produce different results for the total phosphorus data. At James 1, the control was different from Day 1 and Day 7(frozen), while at James 2, the control was different from all other treatments. At York 1, the control was different from both freezing treatments, and at York 2, the control was slightly different from Holding Time. The composite control was similar to both freezing treatments at James 2 and York 1, but was different from both at James 1 and York 2.

The total phosphorus data seemed to be nearly normally distributed, but had unequal variances. Nonparametric statistics showed differences between treatments similar to those found in the parametric statistics.

Suspended Solids

Figures B38-B41 show that frozen sample concentrations did not generally fall within the range defined by the approved treatments.

Results of statistical analyses are shown in Table 12. The control differed from Day 1 at James 1 and the York stations; it differed from Day 7(frozen) at James 2 and York 1; it differed from Day 28(frozen) at York 2. The composite control did not differ from either freezing treatment at any station.

Suspended solids data appeared to be normally distributed, but variances were not homogeneous. Nonparametric statistics indicated that Day 0 differed from Day 1 at James 1, from Day 7(frozen) at James 2 and York 1, and from Day 28(frozen) at York 2.

Silica

Figures B42-B45 show that frozen sample silica concentrations were generally not similar to other treatments. At the James stations, frozen sample concentrations were much lower than other treatment concentrations. At York 2, the Day 7(frozen) sample concentration was much higher than other treatment concentrations.

Results of statistical analyses are shown in Table 13. There appears to be quite a bit of statistically significant variation between treatments for the silica data. The control was different from Day 28(frozen) at all stations, from Day 7(frozen) at all except York 1, and from Holding Time at all except York 2. The composite control was different from both freezing treatments at all stations. In all cases, statistically significant differences between means were also measurable differences.

Table 5. Results of Statistical Analyses: Nitrite

TEST	TREATMENT	STATION James 1	James 2	York 1	York 2
Paired t-test	Day 1	NS	.002	NS	<.001
	Hold Time	<.001	<.001	<.001	<.001
	Day 7-frz	<.001	<.001	<.001	<.001
	Day 28-frz	<.001	.018	.005	<.001
One-way Analysis of Variance		<.0001	<.0001	<.0001	<.0001
Dunnett's Multiple Comparisons	Day 1	.	**#	.	**
	Hold Time	**	**	**	**
	Day 7-frz	**#	**	**#	**
	Day 28-frz	**	**#	**#	**
Scheffe's Multiple Contrasts	Day 7-frz	*#	*#	*#	**
	Day 28-frz	**#	.	.	**#
Kruskal-Wallis Nonparametric ANOVA		<.0001	<.0001	<.0001	<.0001

		James 1				James 2				York 1				York 2			
		D0	D1	HT	D7f	D0	D1	HT	D7f	D0	D1	HT	D7f	D0	D1	HT	D7f
Tukey's Multiple Comparisons	Day 1	.				*#				.				*			
	Hold Time	*	*			*	*#			*	*			*	*		
	D7-frz	*#	*#	*		*	*#	.		*#	*#	*#		*	*	*	
	D28-frz	*	*#	*	.	*#	.	*	*	*#	*#	*#	.	*	*	*	*#
Dunn's Non-parametric Multiple Comparisons	Day 1	.				.				.				.			
	Hold Time	*	*			*	*			*	*			*	*		
	D7-frz	*	*	.		*	*	.		*	*	.		*	*	.	
	D28-frz	*	*	.	.	.	.	*	*	.	.	*	.	.	*	*	.

Probability of getting test statistic at least as large as that calculated if null hypothesis true is shown.
* = significant difference between means (alpha=0.05)
** = significant difference between means (alpha=0.01)
. or NS = no significant difference between means (alpha=0.05)
= difference is not measurable

Table 6. Results of Statistical Analyses: Nitrate-Nitrite

TEST	TREATMENT	STATION James 1	James 2	York 1	York 2
Paired t-test	Day 1	NS	NS	NS	.001
	Hold Time	NS	NS	NS	m
	Day 7-frz	.025	<.001	.005	<.001
	Day 28-frz	.003	NS	<.001	.002
One-way Analysis of Variance		.0001	.0011	.0015	<.0001
Dunnett's Multiple Comparisons	Day 1	.	.	.	**
	Hold Time	.	.	.	m
	Day 7-frz	.	**	.	**
	Day 28-frz	**	.	**	**
Scheffe's Multiple Contrasts	Day 7-frz	.	**	.	**
	Day 28-frz	**	.	**	*
Kruskal-Wallis Nonparametric ANOVA		.0003	.0001	.0025	.0001

		James 1					James 2					York 1					York 2				
		D0	D1	HT	D7f		D0	D1	HT	D7f		D0	D1	HT	D7f		D0	D1	HT	D7f	
Tukey's Multiple Comparisons	Day 1	.					.					.					*				
	Hold Time	.	.				.	.				.	.				m	m			
	D7-frz	.	.	.			*	.	*			.	.	.			*	.	m		
	D28-frz	*	*	*	*		.	.	.	.		*	*	*	.		*	.	m	.	
Dunn's Non-parametric Multiple Comparisons	Day 1	.					.					.					.				
	Hold Time	.	.				.	.				.	.				m	m			
	D7-frz	.	.	.			*	*	*			.	.	.			*	.	m		
	D28-frz	.	.	*	*		.	.	.	*		*	*	.	.		*	.	m	.	

Probability of getting test statistic at least as large as that calculated if null hypothesis true is shown.
* = significant difference between means (alpha=0.05)
** = significant difference between means (alpha=0.01)
. or NS = no significant difference between means (alpha=0.05)
m = missing data group

Table 7. Results of Statistical Analyses: Ammonia

TEST	TREATMENT	STATION James 1	James 2	York 1	York 2
Paired t-test	Day 1	NS	NS	.035	NS
	Hold Time	NS	NS	NS	m
	Day 7-frz	NS	NS	.022	NS
	Day 28-frz	NS	NS	NS	<.001
One-way Analysis of Variance		NS	NS	.0003	<.0001
Dunnett's Multiple Comparisons	Day 1	.	.	*	.
	Hold Time	.	.	.	m
	Day 7-frz	.	.	.	.
	Day 28-frz	.	.	.	**
Scheffe's Multiple Contrasts	Day 7-frz	.	.	*	.
	Day 28-frz	.	.	*#	**
Kruskal-Wallis Nonparametric ANOVA		NS	NS	.0003	<.0001

		James 1				James 2				York 1				York 2			
		D0	D1	HT	D7f	D0	D1	HT	D7f	D0	D1	HT	D7f	D0	D1	HT	D7f
Tukey's Multiple Comparisons	Day 1	.				.				.				.			
	Hold Time	.	.			.	.			.	*			m	m		
	D7-frz	.	.	.		.	.	.		.	*	.		.	.	m	
	D28-frz	.	.	.	.	.	.	.	.	.	.	.	*	*	*	m	*
Dunn's Non-parametric Multiple Comparisons	Day 1	.				.				*				.			
	Hold Time	.	.			.	.			.	*			m	m		
	D7-frz	.	.	.		.	.	.		.	*	.		.	.	m	
	D28-frz	.	.	.	.	.	.	.	.	.	.	.	.	*	*	m	*

Probability of getting test statistic at least as large as that calculated if null hypothesis true is shown.
* = significant difference between means (alpha=0.05)
** = significant difference between means (alpha=0.01)
. or NS = no significant difference between means (alpha=0.05)
--- = no variance in data group
m = missing data group
# = difference is not measurable

Table 8. Results of Statistical Analyses: Total Kjeldahl Nitrogen

TEST	TREATMENT	STATION James 1	James 2	York 1	York 2
Paired t-test	Day 1	.005	.046	NS	NS
	Hold Time	.001 (only one sig.)	NS	NS	NS
	Day 7-frz	.020	NS	NS	NS
	Day 28-frz	NS	NS	NS	NS
One-way Analysis of Variance		<.0001	NS	NS	NS
Dunnett's Multiple Comparisons	Day 1	*	.	.	.
	Hold Time	**	.	.	.
	Day 7-frz	**	.	.	.
	Day 28-frz	.	.	.	.
Scheffe's Multiple Contrasts	Day 7-frz	.	.	.	.
	Day 28-frz	.	.	.	.
Kruskal-Wallis Nonparametric ANOVA		<.0001	NS	NS	.0118

		James 1				James 2				York 1				York 2			
		D0	D1	HT	D7f	D0	D1	HT	D7f	D0	D1	HT	D7f	D0	D1	HT	D7f
Tukey's Multiple Comparisons Procedure	Day 1	*				.				.				.			
	Hold Time	*	.			.	.			.	.			.	.		
	D7-frz	*	.	.		.	.	.		.	.	.		.	.	.	
	D28-frz	.	.	*	*	.	.	.	.	.	.	.	.	.	.	.	.
Dunn's Non-parametric Multiple Comparisons	Day 1	.				.				.				.			
	Hold Time	*	.			.	.			.	.			.	.		
	D7-frz	*	.	.		.	.	.		.	.	.		.	.	*	
	D28-frz	.	.	*	*	.	.	.	.	.	.	.	.	.	.	.	.

Probability of getting test statistic at least as large as that calculated if null hypothesis true is shown.
* = significant difference between means (alpha=0.05)
** = significant difference between means (alpha=0.01)
. or NS = no significant difference between means (alpha=0.05)

Table 9. Results of Statistical Analyses: Orthophosphate

TEST	TREATMENT	STATION James 1	James 2	York 1	York 2
Paired t-test	Day 1	NS	.020	---	.014
	Hold Time	NS	.002	---	.005
	Day 7-frz	---	NS	---	NS
	Day 28-frz	NS	.014	---	<.001
One-way Analysis of Variance		.0001	<.0001	.0001	<.0001
Dunnett's Multiple Comparisons	Day 1	*#	*#	**#	.
	Hold Time	.	**	.	**
	Day 7-frz	.	*#	.	.
	Day 28-frz	**#	*#	.	**
Scheffe's Multiple Contrasts	Day 7-frz	.	.	.	.
	Day 28-frz	**#	**	.	**
Kruskal-Wallis Nonparametric ANOVA		.0001	<.0001	.0001	<.0001

		James 1				James 2				York 1				York 2			
		D0	D1	HT	D7f	D0	D1	HT	D7f	D0	D1	HT	D7f	D0	D1	HT	D7f
Tukey's Multiple Comparisons	Day 1	.				.				*#				.			
	Hold Time	.	.			*	.			.	*#			*	.		
	D7-frz	.	.	.		.	.	.		.	*#	.		.	.	*	
	D28-frz	*#	*#	*#	.	.	*	*	*	.	*#	.	.	*	*	*	*
Dunn's Non-parametric Multiple Comparisons	Day 1	.				.				*				.			
	Hold Time	.	.			.	.			.	*			*	.		
	D7-frz	.	.	.		.	.	.		.	.	.		.	.	*	
	D28-frz	.	*	.	.	.	*	*	*	.	*	.	.	.	*	*	.

Probability of getting test statistic at least as large as that calculated if null hypothesis is true is shown.
* = significant difference between means (alpha=0.05)
** = significant difference between means (alpha=0.01)
. or NS = no significant difference between means (alpha=0.05)
--- = no variance in data group
= difference is not measurable

Table 10. Results of Statistical Analyses: Total Dissolved Phosphorus

TEST	TREATMENT	STATION James 1	James 2	York 1	York 2
Paired t-test	Day 1	NS	.003	NS	NS
	Hold Time	NS	NS	NS	<.001
	Day 7-frz	NS	NS	NS	<.001
	Day 28-frz	NS	NS	NS	<.001
One-way Analysis of Variance		NS	.0012	NS	<.0001
Dunnett's Multiple Comparisons	Day 1	.	**	.	.
	Hold Time	.	.	.	**
	Day 7-frz	.	.	.	**
	Day 28-frz	.	.	.	**
Scheffe's Multiple Contrasts	Day 7-frz	.	.	.	.
	Day 28-frz	.	.	.	**
Kruskal-Wallis Nonparametric ANOVA		.0025	<.0001	<.0001	<.0001

		James 1				James 2				York 1				York 2			
		D0	D1	HT	D7f	D0	D1	HT	D7f	D0	D1	HT	D7f	D0	D1	HT	D7f
Tukey's Multiple Comparisons	Day 1	.				*				.				.			
	Hold Time	.	.			.	*			.	.			*	*		
	D7-frz	.	.	.		.	*	.		.	.	.		*	*	*	
	D28-frz	.	.	.	.	.	.	.	.	.	.	.	.	*	*	*	*
Dunn's Non-parametric Multiple Comparisons	Day 1	.				*				.				.			
	Hold Time	.	.			.	*			*	*			*	*		
	D7-frz	.	*	.		.	*	.		.	.	*		.	.	.	
	D28-frz	.	.	.	.	.	.	*	.	.	.	.	.	*	.	*	*

Probability of getting test statistic at least as large as that calculated if null hypothesis true is shown.
* = significant difference between means (alpha=0.05)
** = significant difference between means (alpha=0.01)
. or NS = no significant difference between means (alpha=0.05)

Table 11. Results of Statistical Analyses: Total Phosphorus

TEST	TREATMENT	STATION James 1	James 2	York 1	York 2
Paired t-test	Day 1	NS	<.001	NS	NS
	Hold Time	NS	<.001	.033	.009
	Day 7-frz	<.001	<.001	<.001	NS
	Day 28-frz	<.001	<.001	<.001	.023
One-way Analysis of Variance		.002	<.0001	<.0001	.0001
Dunnett's Multiple Comparisons	Day 1	**	**	.	.
	Hold Time	.	**	.	*
	Day 7-frz	**	**	**	.
	Day 28-frz	.	**	**	.
Scheffe's Multiple Contrasts	Day 7-frz	.	**	**	.
	Day 28-frz	.	**	**	.
Kruskal-Wallis Nonparametric ANOVA		<.0001	<.0001	<.0001	<.0001

		James 1				James 2				York 1				York 2			
		D0	D1	HT	D7f	D0	D1	HT	D7f	D0	D1	HT	D7f	D0	D1	HT	D7f
Tukey's Multiple Comparisons	Day 1	*				*				.				.			
	Hold Time	.	*			*	.			.	.			.	*		
	D7-frz	*	.	*		*	.	.		*	*	*		.	.	.	
	D28-frz	.	.	.	.	*	*	*	*	*	*	*	*	.	.	*	.
Dunn's Non-parametric Multiple Comparisons	Day 1	*				*				.				.			
	Hold Time	.	*			.	.			.	.			.	*		
	D7-frz	*	.	*		*	.	.		*	*	*		.	.	.	
	D28-frz	.	.	.	.	*	.	*	.	.	*	*	.	.	.	*	.

Probability of getting test statistic at least as large as that calculated if null hypothesis true is shown.
* = significant difference between means (alpha=0.05)
** = significant difference between means (alpha=0.01)
. or NS = no significant difference between means (alpha=0.05)

Table 12. Results of Statistical Analyses: Suspended Solids

TEST	TREATMENT	STATION James 1	James 2	York 1	York 2
Paired t-test	Day 1	.002	.021	NS	NS
	Hold Time	NS	.006	NS	NS
	Day 7-frz	NS	.006	NS	NS
	Day 28-frz	NS	NS	NS	.018
One-way Analysis of Variance		.0078	.0259	.0091	.0057
Dunnett's Multiple Comparisons	Day 1	*	.	*	**
	Hold Time	.	.	.	.
	Day 7-frz	.	**	**	.
	Day 28-frz	.	.	.	**
Scheffe's Multiple Contrasts	Day 7-frz	.	.	.	.
	Day 28-frz	.	.	.	.
Kruskal-Wallis Nonparametric ANOVA		.0037	.0128	.0028	.0069

		James 1				James 2				York 1				York 2			
		D0	D1	HT	D7f	D0	D1	HT	D7f	D0	D1	HT	D7f	D0	D1	HT	D7f
Tukey's Multiple Comparisons	Day 1	*				.				.				*			
	Hold Time	.	.			.	.			.	.			.	.		
	D7-frz	.	.	.		*	.	.		*	.	.		.	.	.	
	D28-frz	.	*	.	.	.	.	.	.	.	.	.	.	*	.	.	.
Dunn's Non-parametric Multiple Comparisons	Day 1	*				.				.				.			
	Hold Time	.	.			.	.			.	.			.	.		
	D7-frz	.	.	.		*	.	.		*	.	*		.	.	.	
	D28-frz	.	*	.	.	.	.	.	.	.	.	.	.	*	.	.	.

Probability of getting test statistic at least as large as that calculated if null hypothesis true is shown.
* = significant difference between means (alpha=0.05)
** = significant difference between means (alpha=0.01)
. or NS = no significant difference between means (alpha=0.05)

Table 13. Results of Statistical Analyses: Silica

TEST	TREATMENT	STATION James 1	James 2	York 1	York 2
Paired t-test	Day 1	<.001	NS	NS	NS
	Hold Time	<.001	<.001	.008	NS
	Day 7-frz	<.001	<.001	.018	<.001
	Day 28-frz	<.001	<.001	<.001	<.001
One-way Analysis of Variance		<.0001	<.0001	<.0001	<.0001
Dunnett's Multiple Comparisons	Day 1	**	.	.	.
	Hold Time	**	**	**	.
	Day 7-frz	**	**	.	**
	Day 28-frz	**	**	**	**
Scheffe's Multiple Contrasts	Day 7-frz	**	**	**	**
	Day 28-frz	**	**	**	**
Kruskal-Wallis Nonparametric ANOVA		<.0001	<.0001	<.0001	<.0001

		James 1				James 2				York 1				York 2			
		D0	D1	HT	D7f	D0	D1	HT	D7f	D0	D1	HT	D7f	D0	D1	HT	D7f
Tukey's Multiple Comparisons	Day 1	*				.				.				.			
	Hold Time	*	*			*	*			*	*			.	.		
	D7-frz	*	*	*		*	*	*		.	*	.		*	*	*	
	D28-frz	*	*	*	*	*	*	*	*	*	*	.	.	*	*	*	*
Dunn's Non-parametric Multiple Comparisons	Day 1	.				.				.				.			
	Hold Time	.	*			.	.			.	.			.	.		
	D7-frz	*	*	.		*	*	.		.	.	.		*	*	*	
	D28-frz	*	*	*	.	*	*	*	.	*	*	.	*	*	*	*	.

Probability of getting test statistic at least as large as that calculated if null hypothesis true is shown.
* = significant difference between means (alpha=0.05)
** = significant difference between means (alpha=0.01)
. or NS = no significant difference between means (alpha=0.05)

DISCUSSION

The statistical parameters which are of importance are the mean and the variance of the various populations sampled (each combination of station, treatment, and water quality constituent). Power statistics were used in the design of this study to choose the number of replicates that would allow detection of a difference between sample means that is equal to or greater than the standard deviation for the procedure with a 95% confidence level for avoiding type I errors (alpha = 0.05) and a 90% confidence level for avoiding type II errors (beta = 0.10). Stated somewhat differently, the number of replications was chosen to be large so that the estimates of the statistical parameters would be good and small differences between sample means could be detected with a relatively large degree of certainty. In general, this objective has been met.

It is one thing to be able to detect small differences during special studies and quite another to be able to make similar distinctions during the routine operations of a laboratory. For that reason, it seems appropriate to compare the differences between sample means for the various treatments with the variations typically observed in routine lab operations. Therefore, the differences between the means for each treatment and the mean for Day 0 have been listed in Table 14 for each water constituent. Also included in the table is the lowest standard used in each analysis, the number of replicates, and the control limit for daily laboratory quality control for precision in each analysis. The control limit is determined from 20 duplicates for a particular analysis. The limit is calculated by using an EPA recommended method of multiplying the mean of the differences in the duplicates by 3.27. Any duplicates in daily measurements that are greater in difference than this number indicate the procedure is out of control and the samples must be rerun after the problem has been corrected. The control limit is an in-house measure of daily variability within a procedure. It is not a measure of the variability in the same procedure performed at another time. This time variability is caused by recalibration of standards, different

baselines or blanks, different reagents, and sometimes different technicians.

The Data Sets

A data point was omitted only when it was known that it was in error or if the replicate or sample were lost. There has been no attempt to remove possible outliers. The raw data is listed in Appendix A. Below are presented, on an analysis by analysis basis, comments about the raw data. It is to be noted from Table 14 that in most cases the difference in mean of each treatment from the mean for Day 0 is less than the control limits for precision in the laboratory.

Nitrite - The nitrite data set is complete. Reference to Table 1 shows that all four stations were spiked with NO2 to insure values above the lowest standard. The differences between the Day 0 mean and each of the freezing treatment means for stations James 1, James 2, and York 1 are roughly equal to the control limit for precision. The mean differences between Day 0 mean and other treatment means for York 2 were several times the control limit. This was the station with the highest spike value.

Nitrate-Nitrite - The sample for York 2 station for holding time for this analysis was not preserved with H2SO4. This was discovered when the samples were being brought to a pH of 7 to be run. The samples were run out of curiosity but the values were about half the value of Day 0.

A replicate was lost in the James 2/Day 1 set. This set had read off scale and had to be diluted. One of the replicates had not been correctly diluted.

All stations included the spiking done with nitrite. All differences between treatment means and day 0 mean were within the control limits for precision except James 1/Day 28(frozen) and James 2/Day 7(frozen).

TABLE 14 DIFFERENCE IN MEAN OF EACH TREATMENT FROM MEAN FOR DAY 0
(Concentrations in mg/l)

	STATION			
NITRITE	J1	J2	Y1	Y2
Replicates = 13				
Lowest Standard = 0.005				
Upper Control Limit = 0.001				
DAY 1	0.0001	0.0007	0.0002	-0.0020
HT	0.0022	0.0017	0.0017	0.0099
FREEZE 7	0.0009	0.0017	0.0010	0.0042
FREEZE 28	0.0011	0.0005	0.0007	0.0034
NITRATE - NITRITE				
Replicates = 13				
Lowest Standard = 0.010				
Upper Control Limit = 0.007				
DAY 1	0.0002	0.0011	0.0005	0.0028
HT	-0.0008	-0.0039	0.0008	-.----
FREEZE 7	-0.0021	0.0105	0.0018	0.0051
FREEZE 28	0.0084	0.0020	0.0044	0.0040
AMMONIA				
Replicates = 13				
Lowest Standard = 0.010				
Upper Control Limit = 0.007				
DAY 1	0.0019	-0.0011	0.0029	0.0008
HT	0.0015	-0.0014	-0.0013	-.----
FREEZE 7	0.0015	-0.0007	-0.0026	0.0020
FREEZE 28	0.0001	-0.0010	0.0012	0.0129
TOTAL KJELDAHL NITROGEN				
Replicates = 8				
Lowest Standard = 0.025				
Upper Control Limit = 0.050				
DAY 1	-0.0456	0.0448	0.0286	-0.0424
HT	-0.0876	0.0086	0.0262	-0.0323
FREEZE 7	-0.0796	0.0172	0.0218	0.0244
FREEZE 28	-0.0125	0.0298	-0.0033	0.0202

TABLE 14 (Continued)

DIFFERENCE IN MEAN OF EACH TREATMENT FROM MEAN FOR DAY 0
(Concentration in mg/l)

	STATION			
SILICA	J1	J2	Y1	Y2
Replicates = 13				
Lowest Standard = 0.056				
Upper Control Limit = 0.010				
DAY 1	-0.0137	0.0030	0.0015	-0.0015
HT	0.0092	0.0126	-0.0037	-0.0006
FREEZE 7	0.0142	0.0552	-0.0024	-0.1275
FREEZE 28	0.0697	0.1776	-0.0058	-0.0229
TOTAL SUSPENDED SOLIDS				
Replicates = 10				
Lower Limit = 4				
Upper Control Limit = 12				
DAY 1	2.2	2.8	2.2	1.7
HT	1.0	2.7	0.4	0.7
FREEZE 7	1.2	3.9	2.8	0.8
FREEZE 28	-0.6	1.3	1.3	1.9
ORTHOPHOSPHATE				
Replicates = 13				
Lowest Standard = 0.010				
Upper Control Limit = 0.003				
DAY 1	0.0004	0.0008	0.0008	-0.0008
HT	0.0000	0.0015	-0.0002	-0.0017
FREEZE 7	-0.0001	0.0008	0.0002	0.0002
FREEZE 28	-0.0006	-0.0008	0.0000	0.0024
TOTAL DISSOLVED PHOSPHORUS				
Replicates =13				
Lowest Standard = 0.010				
Upper Control Limit = 0.005				
DAY 1	-0.0004	0.0029	0.0008	0.0005
HT	-0.0013	-0.0013	-0.0015	-0.0048
FREEZE 7	-0.0040	-0.0004	0.0006	-0.0027
FREEZE 28	-0.0003	0.0012	0.0004	0.0052
TOTAL PHOSPHORUS				
Replicates = 13				
Lowest Standard = 0.010				
Upper Control Limit = 0.005				
DAY 1	0.0035	0.0258	0.0010	0.0016
HT	0.0002	0.0224	0.0011	-0.0020
FREEZE 7	0.0037	0.0235	-0.0070	0.0000
FREEZE 28	0.0022	0.0333	-0.0037	0.0019

Ammonia - The sample for York 2 station for holding time was the same as the nitrate-nitrite and suffered the same problem; no H_2SO_4 was added to the sample for preservative.

James 1/Day 0, is missing a data point because one of the replicates was not analysed.

The two York River stations were spiked in order to read above the lowest standard. The data for the James stations were much lower in value than expected. This data was so low in ammonia as to be of doubtful statistical value. All differences between treatment means and Day 0 mean were within the control limit for precision except the York 2/Day 28(frozen) sample.

Total Kjeldahl Nitrogen - The one missing data point in the James 1/frozen 7 days data set was due to a broken flask. The data reflect the ammonia spikes in the York River samples. One data point in the York 2/Day one set is questionable (0.801), but there was no known reason for this anomalous value. All differences between treatment means and Day 0 mean were within the control limit for precision except James 1/holding time and James 1/Day 7.

Silica - Silica was not spiked and the values for York 1 were below the lowest standard. The data sets are all complete. The data in York 2/Day 7(frozen), is more than twice the value of the other treatments. A possible cause is that insufficient time after thawing was allowed, but that is uncertain. Sample means for James 1/Day 28(frozen), James 2/Day 28(frozen), and York 2/Day 7(frozen) have a greater difference from Day 0 than the control limit for precision.

Total Suspended Solids - Except for the James 2 station, the total suspended solid concentrations were low. The data for two replicates were lost due to filters being torn after filtering. None of the treatment means showed a difference from Day 0 mean greater than the control limit for precision.

Orthophosphate - This data set is complete. Low values were expected in the York River and these samples were spiked. The values

for York 1 were still below the lowest standard. It has been observed that when adding phosphate to a large container of water, the amount measured is always less than the amount originally added. This could be due to biological activity or adsorption onto the walls of the container. This was not taken into account in determining the amount of phosphate added. None of the treatment means showed a difference from Day 0 mean greater than the control limit for precision.

Total Dissolved Phosphorus - This data set is complete. The York River values reflect the spiking of the samples for orthophosphate. None of the treatment means showed a difference from Day 0 mean greater than the control limit for precision.

Total Phophorus - This data set is complete. The York River values reflect the spiking of the samples for orthophosphate. The value for James 2/Day 0, is about 20% higher than the other treatments. It is possible that the container was contaminated, but this is uncertain. All other treatment means have a difference from Day 0 mean less than the control limit for precision.

CONCLUSIONS

This study was designed with power statistics so that the number of replicates (13) was sufficient to detect small differences between treatments. The volume of water required and the equipment limited the replicates in TSS and TKN analyses (10 and 8 respectively).

The difference between treatments was measurable and statistically significant in a number of cases. The difference between the immediate analysis and the frozen samples was generally less than the daily control limits in the laboratory for precision. Therefore, in our opinion, the difference was not a practical one.

An additional source of variability was created by performing the analyses on different days. Performing an analysis at another time introduces new calibration standards, possible new reagents, new baselines or blanks, and sometimes different technicians. This variability has not been quantified, but its magnitude is expected to be similar to that of interlaboratory variability.

Except for silica, freezing had no practical effect on the concentration levels measured in the laboratory. Freezing is known to cause difficulties for silica measurements; for 3 out of 4 stations in this study the difference between treatment means was greater than the control limit for precision. It is suggested that samples to be analysed for this constituent not be frozen as a method of preservation, particularly in estuaries and fresh water.

Although the differences in means between immediate analysis and either of the freezing treatments was statistically significant, that difference generally was less than the laboratory control limit for precision. The difference between means may have been greater than the control limit for one out of the four samples, but this was also true for the EPA - recommended treatments.

The procedure for total suspended solids requires a large volume of water. When a large number of replicates are being processed, the volume required is incredible. The results of this study suggest that freezing does not affect the measurements. However, given the 7 day holding time, there usually is no need to freeze these samples.

REFERENCES

MacDonald, R.W. and F.A. McLaughlin (1982) "The effect of storage by freezing on dissolved inorganic phosphate, nitrate and reactive silicate for samples from coastal and estuarine waters". Water Research 16:95-104.

Nie, Norman H. (1975) SPSS: Statistical Package for the Social Sciences. 2nd ed. 675pp. McGraw-Hill Book Co. NY.

SPSS Inc. (1986) SPSSX User's Guide. 2nd ed. 988 pp. McGraw-Hill Book Co. NY.

Standard Methods for the Examination of Water and Wastewater (1975) 14th ed. 1193pp. American Public Health Association. Washington,DC.

Strickland, J.D.H. and T.R. Parsons (1972) A Practical Handbook of Seawater Analysis. Fisheries Research Board of Canada. Bulletin 167.

Technicon Industrial Method No. 186-72W, Silicates in Water and Seawater, (1973). Technicon Instruments Corp. Ardsley, NY.

U.S. Environmental Protection Agency. (1979) Methods for Chemical Analysis of Water and Wastes. National Environmental Research Center. Cincinnati, OH.

Zar, Jerrold H. (1984) Biostatistical Analysis. 2nd ed. 718pp. Prentice-Hall, Inc. Englewood Cliffs, NJ.

APPENDICES

A. Raw Data

B. Graphical Summaries of Raw Data

C. Results of Statistical Analyses

D. Laboratory Methods

APPENDIX A

Raw Data

CONTENTS:

TABLE A.1 NITRITE DATA FOR FREEZING STUDY
(concentration in mg/l)

STATION	DAY ZERO	DAY ONE	HOLDING TIME	FROZEN 7 DAYS	FROZEN 28 DAYS
'JAMES 1'					
	.010	.010	.008	.009	.009
	.010	.010	.007	.009	.009
	.010	.009	.007	.009	.009
	.010	.010	.008	.009	.009
	.010	.010	.008	.009	.009
	.010	.010	.008	.009	.009
	.010	.010	.008	.009	.009
	.010	.010	.008	.009	.009
	.010	.010	.008	.009	.009
	.010	.010	.008	.009	.009
	.010	.010	.008	.009	.009
	.010	.010	.008	.009	.008
	.010	.010	.008	.009	.009
MIN	.010	.009	.007	.009	.008
MAX	.010	.010	.008	.009	.009
MEAN	.010	.010	.008	.009	.009
STDEV	.000	.000	.000	.000	.000
'JAMES 2'					
	.007	.006	.006	.005	.007
	.007	.007	.005	.005	.007
	.007	.006	.006	.005	.007
	.008	.006	.006	.006	.007
	.008	.007	.006	.006	.007
	.008	.007	.006	.006	.007
	.008	.007	.006	.006	.007
	.007	.007	.005	.006	.007
	.007	.007	.006	.006	.007
	.007	.007	.006	.006	.007
	.008	.007	.006	.006	.007
	.007	.007	.006	.006	.007
	.008	.007	.006	.006	.007
MIN	.007	.006	.005	.005	.007
MAX	.008	.007	.006	.006	.007
MEAN	.007	.007	.006	.006	.007
STDEV	.001	.000	.000	.000	.000

TABLE A.1 (continued)

NITRITE DATA FOR FREEZING STUDY
(concentration in mg/l)

STATION	DAY ZERO	DAY ONE	HOLDING TIME	FROZEN 7 DAYS	FROZEN 28 DAYS
'YORK 1'					
	.011	.011	.009	.010	.010
	.011	.010	.009	.010	.010
	.011	.011	.009	.010	.010
	.011	.010	.009	.010	.010
	.011	.011	.009	.010	.010
	.011	.011	.009	.010	.010
	.011	.011	.009	.010	.010
	.011	.011	.009	.010	.010
	.011	.011	.009	.010	.011
	.011	.011	.010	.010	.011
	.011	.011	.010	.010	.011
	.011	.011	.010	.010	.010
	.011	.011	.010	.010	.011
MIN	.011	.010	.009	.010	.010
MAX	.011	.011	.010	.010	.011
MEAN	.011	.011	.009	.010	.010
STDEV	.000	.000	.000	.000	.000
'YORK 2'					
	.054	.055	.044	.050	.051
	.054	.056	.044	.050	.051
	.054	.058	.044	.051	.051
	.055	.056	.045	.050	.051
	.055	.056	.044	.050	.052
	.055	.056	.044	.050	.051
	.054	.056	.044	.051	.051
	.054	.058	.045	.050	.051
	.055	.057	.045	.051	.051
	.055	.058	.045	.050	.051
	.054	.056	.046	.050	.051
	.054	.056	.045	.050	.051
	.055	.056	.045	.051	.051
MIN	.054	.055	.044	.050	.051
MAX	.055	.058	.046	.051	.052
MEAN	.054	.056	.045	.050	.051
STDEV	.001	.001	.001	.000	.000

TABLE A.2 NITRITE-NITRATE DATA FOR FREEZING STUDY
(concentration in mg/l)

STATION	DAY ZERO	DAY ONE	HOLDING TIME	FROZEN 7 DAYS	FROZEN 28 DAYS
'JAMES 1'					
	.177	.174	.196	.178	.178
	.179	.181	.162	.179	.180
	.176	.178	.166	.183	.171
	.176	.182	.183	.183	.178
	.181	.180	.184	.183	.171
	.182	.179	.180	.181	.166
	.184	.179	.180	.184	.185
	.177	.179	.182	.183	.173
	.182	.179	.184	.181	.166
	.181	.179	.184	.182	.163
	.177	.182	.180	.181	.156
	.181	.180	.182	.181	.164
	.182	.180	.182	.183	.174
MIN	.176	.174	.162	.178	.156
MAX	.184	.182	.196	.184	.185
MEAN	.180	.179	.180	.182	.171
STDEV	.003	.002	.008	.002	.008
'JAMES 2'					
	.265	.261	.249	.251	.242
	.269	.270	.256	.257	.286
	.266	.271	.270	.261	.273
	.264	.268	.274	.263	.261
	.263	.263	.274	.257	.266
	.263	.268	.274	.258	.272
	.261	.268	.274	.256	.281
	.276	.268	.305	.258	.274
	.276	.262	.277	.258	.267
	.274	.270	.273	.258	.254
	.267	.266	.269	.258	.266
	.272	.268	.269	.261	.260
	.272	.---	.275	.256	.260
MIN	.261	.261	.249	.251	.242
MAX	.276	.271	.305	.263	.286
MEAN	.268	.267	.272	.258	.266
STDEV	.005	.003	.013	.003	.012

TABLE A.2 (continued) NITRITE-NITRATE DATA FOR FREEZING STUDY
(concentration in mg/l)

STATION	DAY ZERO	DAY ONE	HOLDING TIME	FROZEN 7 DAYS	FROZEN 28 DAYS
"YORK 1"					
	.108	.102	.108	.104	.102
	.113	.107	.102	.108	.102
	.110	.108	.105	.108	.104
	.110	.110	.109	.107	.105
	.110	.111	.104	.108	.110
	.109	.111	.108	.109	.106
	.110	.110	.115	.110	.104
	.109	.108	.118	.106	.108
	.111	.111	.111	.108	.105
	.109	.111	.111	.109	.102
	.107	.110	.105	.108	.105
	.110	.108	.112	.108	.111
	.109	.111	.106	.109	.103
MIN	.107	.102	.102	.104	.102
MAX	.113	.111	.118	.110	.111
MEAN	.110	.109	.109	.108	.105
STDEV	.001	.003	.005	.002	.003
"YORK 2"					
	.073	.074	.---	.074	.070
	.076	.074	.---	.075	.072
	.079	.076	.---	.075	.081
	.080	.076	.---	.073	.079
	.079	.080	.---	.074	.079
	.081	.077	.---	.074	.072
	.082	.077	.---	.074	.076
	.082	.077	.---	.074	.079
	.080	.077	.---	.074	.075
	.081	.077	.---	.074	.071
	.082	.076	.---	.074	.073
	.080	.077	.---	.074	.077
	.076	.076	.---	.075	.075
MIN	.073	.074	M	.073	.070
MAX	.082	.080	M	.075	.081
MEAN	.079	.076	M	.074	.075
STDEV	.003	.002	M	.001	.004

TABLE A.3 AMMONIA DATA FOR FREEZING STUDY
(concentration in mg/l)

STATION	DAY ZERO	DAY ONE	HOLDING TIME	FROZEN 7 DAYS	FROZEN 28 DAYS
'JAMES 1'					
	.002	.001	.005	.009	.006
	.001	.003	.005	.001	.002
	.002	.003	.005	.007	.002
	.002	.004	.007	.004	.000
	.003	.005	.007	.005	.003
	.015	.008	.002	.006	.005
	.---	.003	.002	.004	.004
	.002	.004	.002	.003	.007
	.005	.001	.002	.001	.006
	.005	.003	.000	.000	.004
	.008	.003	.002	.000	.009
	.007	.000	.003	.000	.009
	.009	.003	.003	.007	.007
MIN	.001	.000	.000	.000	.000
MAX	.015	.008	.007	.009	.009
MEAN	.005	.003	.003	.004	.005
STDEV	.004	.002	.002	.003	.003
'JAMES 2'					
	.002	.002	.010	.007	.000
	.001	.002	.008	.004	.003
	.001	.000	.004	.002	.006
	.002	.003	.003	.002	.002
	.001	.005	.003	.004	.000
	.002	.002	.000	.002	.004
	.000	.001	.003	.002	.001
	.002	.002	.003	.001	.005
	.000	.004	.002	.001	.003
	.000	.007	.000	.001	.003
	.001	.002	.000	.001	.003
	.002	.002	.002	.001	.003
	.006	.002	.000	.001	.000
MIN	.000	.000	.000	.001	.000
MAX	.006	.007	.010	.007	.006
MEAN	.002	.003	.003	.002	.003
STDEV	.002	.002	.003	.002	.002

TABLE A.3 (continued) AMMONIA DATA FOR FREEZING STUDY (concentration in mg/l)

STATION	DAY ZERO	DAY ONE	HOLDING TIME	FROZEN 7 DAYS	FROZEN 28 DAYS
"YORK 1"					
	.014	.008	.022	.021	.009
	.014	.008	.018	.017	.010
	.014	.008	.018	.017	.009
	.012	.009	.020	.020	.010
	.012	.011	.015	.021	.013
	.012	.010	.014	.016	.013
	.012	.010	.013	.012	.013
	.012	.021	.013	.012	.013
	.014	.---	.011	.017	.014
	.014	.009	.010	.013	.014
	.014	.010	.015	.012	.009
	.014	.010	.012	.014	.015
	.014	.010	.008	.014	.014
MIN	.012	.008	.008	.012	.009
MAX	.014	.021	.022	.021	.015
MEAN	.013	.010	.015	.016	.012
STDEV	.001	.003	.004	.003	.002
"YORK 2"					
	.070	.079	.---	.085	.068
	.072	.075	.---	.079	.064
	.075	.080	.---	.075	.065
	.077	.079	.---	.079	.067
	.080	.081	.---	.079	.069
	.083	.080	.---	.077	.065
	.084	.081	.---	.080	.068
	.100	.081	.---	.080	.067
	.084	.080	.---	.076	.069
	.087	.084	.---	.079	.068
	.081	.080	.---	.079	.067
	.080	.081	.---	.079	.071
	.079	.080	.---	.079	.076
MIN	.070	.075	M	.075	.064
MAX	.100	.084	M	.085	.076
MEAN	.081	.080	M	.079	.068
STDEV	.008	.002	M	.002	.003

TABLE A.4 TOTAL KJELDAHL NITROGEN DATA FOR FREEZING STUDY
(concentration in mg/l)

STATION	DAY ZERO	DAY ONE	HOLDING TIME	FROZEN 7 DAYS	FROZEN 28 DAYS
'JAMES 1'					
	.375	.415	.402	.389	.376
	.257	.359	.437	.451	.380
	.340	.421	.444	.400	.368
	.367	.405	.411	.415	.357
	.360	.405	.446	.387	.336
	.370	.405	.462	.434	.380
	.365	.390	.445	.515	.346
	.378	.377	.466	.---	.369
MIN	.257	.359	.402	.387	.336
MAX	.378	.421	.466	.515	.380
MEAN	.351	.397	.439	.427	.364
STDEV	.040	.021	.022	.045	.016
'JAMES 2'					
	.396	.422	.405	.417	.399
	.365	.277	.449	.475	.429
	.516	.440	.483	.453	.432
	.438	.448	.419	.402	.424
	.416	.388	.391	.389	.371
	.460	.327	.423	.396	.392
	.446	.418	.412	.399	.399
	.441	.399	.427	.409	.393
MIN	.365	.277	.391	.389	.371
MAX	.516	.448	.483	.475	.432
MEAN	.435	.390	.426	.417	.405
STDEV	.045	.059	.029	.030	.021

TABLE A.4 (continued) TOTAL KJELDAHL NITROGEN DATA FOR FREEZING STUDY (concentration in mg/l)

STATION	DAY ZERO	DAY ONE	HOLDING TIME	FROZEN 7 DAYS	FROZEN 28 DAYS
'YORK 1'					
	.493	.524	.422	.407	.459
	.408	.383	.464	.509	.479
	.606	.432	.433	.427	.475
	.450	.420	.416	.440	.464
	.450	.411	.421	.424	.455
	.432	.443	.488	.431	.473
	.435	.438	.416	.462	.455
	.436	.430	.440	.435	.476
MIN	.408	.383	.416	.407	.455
MAX	.606	.524	.488	.509	.479
MEAN	.464	.435	.437	.442	.467
STDEV	.062	.041	.026	.031	.010
'YORK 2'					
	.521	.530	.542	.465	.539
	.425	.423	.574	.507	.562
	.520	.534	.572	.487	.554
	.533	.556	.584	.485	.544
	.550	.635	.548	.500	.545
	.571	.801	.558	.542	.543
	.574	.564	.574	.552	.558
	.567	.557	.567	.528	.578
MIN	.425	.423	.542	.465	.539
MAX	.574	.801	.584	.552	.578
MEAN	.533	.575	.565	.508	.553
STDEV	.049	.108	.014	.030	.013

TABLE A.5 SILICA DATA FOR FREEZING STUDY
(concentration in mg/l)

STATION	DAY ZERO	DAY ONE	HOLDING TIME	FROZEN 7 DAYS	FROZEN 28 DAYS
'JAMES 1'					
	.654	.671	.650	.645	.588
	.666	.671	.653	.645	.590
	.659	.673	.650	.645	.594
	.666	.673	.653	.645	.594
	.659	.678	.648	.647	.594
	.666	.678	.653	.645	.594
	.666	.678	.653	.645	.588
	.659	.678	.653	.647	.594
	.659	.678	.650	.649	.594
	.659	.673	.653	.645	.594
	.666	.673	.653	.651	.588
	.659	.673	.650	.649	.585
	.654	.673	.653	.649	.588
MIN	.654	.671	.648	.645	.585
MAX	.666	.678	.653	.651	.594
MEAN	.661	.675	.652	.647	.591
STDEV	.005	.003	.002	.002	.003
'JAMES 2'					
	1.272	1.271	1.247	1.205	1.079
	1.277	1.278	1.259	1.210	1.096
	1.277	1.271	1.264	1.215	1.091
	1.272	1.271	1.267	1.235	1.091
	1.277	1.271	1.272	1.221	1.096
	1.283	1.271	1.259	1.227	1.091
	1.283	1.278	1.259	1.232	1.105
	1.283	1.271	1.267	1.218	1.096
	1.274	1.271	1.267	1.218	1.108
	1.272	1.271	1.267	1.218	1.101
	1.272	1.271	1.267	1.221	1.113
	1.267	1.271	1.259	1.218	1.101
	1.267	1.271	1.259	1.221	1.100
MIN	1.267	1.271	1.247	1.205	1.079
MAX	1.283	1.278	1.272	1.235	1.113
MEAN	1.275	1.272	1.263	1.220	1.098
STDEV	.006	.003	.006	.008	.009

TABLE A.5 (continued)

SILICA DATA FOR FREEZING STUDY
(concentration in mg/l)

STATION	DAY ZERO	DAY ONE	HOLDING TIME	FROZEN 7 DAYS	FROZEN 28 DAYS
"YORK 1"					
	.035	.036	.038	.038	.041
	.035	.031	.042	.038	.046
	.035	.026	.038	.038	.043
	.035	.036	.038	.038	.041
	.035	.033	.038	.038	.039
	.035	.029	.036	.038	.039
	.035	.024	.038	.038	.039
	.035	.036	.042	.038	.039
	.035	.031	.038	.038	.039
	.035	.029	.036	.038	.041
	.042	.040	.036	.034	.039
	.028	.040	.038	.033	.039
	.028	.038	.038	.033	.039
MIN	.028	.024	.036	.033	.039
MAX	.042	.040	.042	.038	.046
MEAN	.034	.033	.038	.037	.040
STDEV	.003	.005	.002	.002	.002
"YORK 2"					
	.067	.064	.063	.189	.087
	.067	.087	.063	.185	.084
	.067	.064	.063	.189	.082
	.067	.059	.063	.194	.082
	.067	.059	.063	.194	.087
	.060	.064	.063	.189	.093
	.060	.064	.067	.194	.080
	.060	.061	.063	.189	.087
	.067	.059	.070	.189	.093
	.060	.068	.063	.189	.084
	.060	.064	.063	.190	.080
	.060	.064	.063	.199	.087
	.060	.064	.063	.189	.093
MIN	.060	.059	.063	.185	.080
MAX	.067	.087	.070	.199	.093
MEAN	.063	.065	.064	.191	.086
STDEV	.004	.007	.002	.004	.005

TABLE A.6 TOTAL SUSPENDED SOLIDS DATA FOR FREEZING STUDY
(concentration in mg/l)

STATION	DAY ZERO	DAY ONE	HOLDING TIME	FROZEN 7 DAYS	FROZEN 28 DAYS
'JAMES 1'					
	15.000	14.000	14.000	16.000	16.000
	15.000	15.000	14.000	15.000	14.000
	15.000	13.000	17.000	14.000	14.000
	17.000	13.000	14.000	14.000	14.000
	17.000	13.000	15.000	13.000	18.000
	17.000	13.000	15.000	15.000	18.000
	13.000	13.000	14.000	14.000	19.000
	15.000	13.000	15.000	15.000	21.000
	16.000	14.000	15.000	15.000	11.000
	17.000	14.000	14.000	14.000	.---
MIN	13.000	13.000	14.000	13.000	11.000
MAX	17.000	15.000	17.000	16.000	21.000
MEAN	15.700	13.500	14.700	14.500	16.111
STDEV	1.337	.707	.949	.850	3.140
'JAMES 2'					
	37.000	34.000	36.000	32.000	33.000
	38.000	28.000	31.000	31.000	34.000
	39.000	36.000	38.000	30.000	37.000
	39.000	37.000	36.000	35.000	39.000
	37.000	37.000	36.000	30.000	37.000
	37.000	38.000	30.000	39.000	40.000
	38.000	33.000	37.000	35.000	31.000
	37.000	35.000	36.000	38.000	41.000
	38.000	34.000	35.000	35.000	37.000
	39.000	39.000	37.000	35.000	37.000
MIN	37.000	28.000	30.000	30.000	31.000
MAX	39.000	39.000	38.000	39.000	41.000
MEAN	37.900	35.100	35.200	34.000	36.600
STDEV	.876	3.143	2.616	3.162	3.134

TABLE A.6 (continued) TOTAL SUSPENDED SOLIDS DATA FOR FREEZING STUDY
(concentration in mg/l)

STATION 'YORK 1'	DAY ZERO	DAY ONE	HOLDING TIME	FROZEN 7 DAYS	FROZEN 28 DAYS
	6.000	6.000	6.000	7.000	6.000
	7.000	6.000	8.000	6.000	8.000
	6.000	6.000	10.000	5.000	7.000
	5.000	6.000	10.000	6.000	9.000
	7.000	7.000	7.000	5.000	7.000
	16.000	5.000	7.000	2.000	5.000
	7.000	5.000	6.000	4.000	6.000
	7.000	5.000	7.000	6.000	8.000
	10.000	7.000	6.000	6.000	3.000
	8.000	4.000	8.000	4.000	7.000
MIN	5.000	4.000	6.000	2.000	3.000
MAX	16.000	7.000	10.000	7.000	9.000
MEAN	7.900	5.700	7.500	5.100	6.600
STDEV	3.143	.949	1.509	1.449	1.713
'YORK 2'					
	17.000	19.000	20.000	18.000	17.000
	17.000	18.000	19.000	19.000	18.000
	20.000	18.000	19.000	19.000	18.000
	22.000	16.000	21.000	18.000	18.000
	20.000	17.000	19.000	19.000	17.000
	19.000	18.000	18.000	19.000	18.000
	19.000	19.000	17.000	19.000	18.000
	21.000	17.000	18.000	19.000	16.000
	19.000	18.000	18.000	19.000	17.000
	19.000	16.000	17.000	16.000	.---
MIN	17.000	16.000	17.000	16.000	16.000
MAX	22.000	19.000	21.000	19.000	18.000
MEAN	19.300	17.600	18.600	18.500	17.444
STDEV	1.567	1.075	1.265	.972	.726

TABLE A.7 ORTHOPHOSPHATE DATA FOR FREEZING STUDY
(concentration in mg/l)

STATION	DAY ZERO	DAY ONE	HOLDING TIME	FROZEN 7 DAYS	FROZEN 28 DAYS
'JAMES 1'					
	.011	.009	.011	.011	.012
	.011	.011	.011	.011	.012
	.011	.011	.011	.011	.012
	.011	.009	.011	.011	.012
	.011	.011	.010	.011	.012
	.011	.011	.011	.011	.012
	.010	.011	.011	.011	.011
	.011	.011	.011	.011	.011
	.011	.011	.011	.011	.012
	.011	.009	.011	.011	.011
	.011	.011	.011	.011	.011
	.011	.011	.011	.011	.011
	.011	.011	.011	.011	.011
MIN	.010	.009	.010	.011	.011
MAX	.011	.011	.011	.011	.012
MEAN	.011	.011	.011	.011	.012
STDEV	.000	.001	.000	.000	.001
'JAMES 2'					
	.013	.013	.013	.014	.015
	.016	.013	.013	.012	.015
	.013	.013	.013	.014	.015
	.013	.013	.013	.014	.014
	.013	.013	.011	.012	.015
	.013	.013	.013	.012	.015
	.013	.013	.011	.014	.014
	.013	.013	.013	.014	.015
	.015	.013	.011	.014	.015
	.015	.015	.013	.012	.015
	.015	.013	.013	.012	.015
	.015	.013	.013	.014	.015
	.015	.013	.013	.014	.015
MIN	.013	.013	.011	.012	.014
MAX	.016	.015	.013	.014	.015
MEAN	.014	.013	.013	.013	.015
STDEV	.001	.001	.001	.001	.000

TABLE A.7 (continued)

ORTHOPHOSPHATE DATA FOR FREEZING STUDY
(concentration in mg/l)

STATION	DAY ZERO	DAY ONE	HOLDING TIME	FROZEN 7 DAYS	FROZEN 28 DAYS
'YORK 1'					
	.005	.004	.005	.004	.005
	.005	.004	.005	.004	.005
	.005	.004	.005	.006	.005
	.005	.004	.005	.004	.005
	.005	.004	.005	.004	.005
	.005	.004	.006	.004	.005
	.005	.004	.005	.004	.005
	.005	.004	.005	.004	.005
	.005	.006	.006	.006	.005
	.005	.004	.005	.006	.005
	.005	.004	.005	.006	.005
	.005	.004	.005	.006	.005
	.005	.004	.006	.004	.005
MIN	.005	.004	.005	.004	.005
MAX	.005	.006	.006	.006	.005
MEAN	.005	.004	.005	.005	.005
STDEV	.000	.001	.000	.001	.000
'YORK 2'					
	.076	.078	.079	.076	.071
	.076	.078	.079	.076	.075
	.078	.078	.079	.076	.075
	.078	.078	.079	.078	.073
	.078	.078	.080	.078	.076
	.076	.078	.080	.076	.075
	.076	.079	.080	.078	.076
	.078	.078	.079	.076	.076
	.078	.078	.080	.078	.078
	.078	.078	.080	.078	.075
	.078	.079	.075	.078	.073
	.078	.079	.079	.078	.076
	.078	.078	.079	.078	.076
MIN	.076	.078	.075	.076	.071
MAX	.078	.079	.080	.078	.078
MEAN	.077	.078	.079	.077	.075
STDEV	.001	.000	.001	.001	.002

TABLE A.8 TOTAL DISSOLVED PHOSPHORUS DATA FOR FREEZING STUDY
(concentration in mg/l)

STATION	DAY ZERO	DAY ONE	HOLDING TIME	FROZEN 7 DAYS	FROZEN 28 DAYS
'JAMES 1'					
	.025	.022	.022	.025	.024
	.022	.020	.022	.033	.024
	.022	.022	.022	.029	.022
	.022	.051	.022	.027	.020
	.022	.020	.041	.023	.024
	.027	.022	.022	.021	.022
	.022	.022	.022	.021	.020
	.025	.020	.022	.023	.028
	.022	.020	.022	.050	.022
	.022	.022	.024	.025	.022
	.022	.020	.024	.023	.022
	.022	.020	.024	.025	.022
	.022	.020	.024	.023	.028
MIN	.022	.020	.022	.021	.020
MAX	.027	.051	.041	.050	.028
MEAN	.023	.023	.024	.027	.023
STDEV	.002	.008	.005	.008	.003
'JAMES 2'					
	.029	.020	.024	.023	.036
	.022	.022	.024	.025	.020
	.022	.022	.024	.023	.020
	.022	.022	.026	.023	.020
	.022	.020	.024	.023	.020
	.025	.020	.024	.027	.020
	.022	.020	.024	.023	.022
	.029	.022	.024	.023	.020
	.022	.020	.024	.027	.022
	.025	.020	.024	.023	.020
	.022	.020	.026	.023	.020
	.022	.020	.026	.023	.024
	.022	.020	.028	.025	.026
MIN	.022	.020	.024	.023	.020
MAX	.029	.022	.028	.027	.036
MEAN	.024	.021	.025	.024	.022
STDEV	.003	.001	.001	.002	.005

TABLE A.8 (continued) TOTAL DISSOLVED PHOSPHORUS DATA FOR FREEZING STUDY (concentration in mg/l)

STATION	DAY ZERO	DAY ONE	HOLDING TIME	FROZEN 7 DAYS	FROZEN 28 DAYS
"YORK 1"					
	.012	.012	.020	.012	.012
	.012	.012	.015	.010	.012
	.012	.012	.015	.012	.014
	.012	.012	.013	.014	.012
	.012	.012	.015	.012	.012
	.014	.014	.015	.012	.012
	.014	.012	.015	.012	.014
	.012	.012	.015	.012	.014
	.012	.012	.013	.012	.014
	.027	.012	.015	.010	.014
	.012	.018	.015	.012	.014
	.014	.012	.015	.012	.012
	.012	.014	.015	.027	.016
MIN	.012	.012	.013	.010	.012
MAX	.027	.018	.020	.027	.016
MEAN	.014	.013	.015	.013	.013
STDEV	.004	.002	.002	.004	.001
"YORK 2"					
	.090	.092	.096	.092	.085
	.090	.090	.096	.092	.087
	.090	.090	.096	.092	.087
	.092	.090	.096	.094	.087
	.092	.090	.096	.094	.085
	.092	.092	.098	.094	.085
	.090	.092	.098	.092	.085
	.090	.090	.096	.094	.089
	.092	.096	.094	.096	.085
	.090	.088	.096	.094	.083
	.094	.088	.094	.100	.085
	.092	.090	.098	.092	.087
	.090	.090	.092	.094	.087
MIN	.090	.088	.092	.092	.083
MAX	.094	.096	.098	.100	.089
MEAN	.091	.091	.096	.094	.086
STDEV	.001	.002	.002	.002	.002

TABLE A.9 TOTAL PHOSPHORUS DATA FOR FREEZING STUDY
(concentration in mg/l)

STATION	DAY ZERO	DAY ONE	HOLDING TIME	FROZEN 7 DAYS	FROZEN 28 DAYS
"JAMES 1"					
	.063	.057	.065	.060	.063
	.065	.059	.063	.060	.063
	.063	.059	.067	.062	.063
	.065	.059	.063	.062	.063
	.065	.061	.065	.062	.063
	.065	.081	.063	.062	.061
	.065	.059	.065	.062	.061
	.065	.061	.065	.060	.061
	.065	.059	.067	.060	.063
	.065	.059	.063	.062	.063
	.063	.059	.065	.058	.063
	.065	.061	.063	.062	.063
	.067	.061	.065	.061	.063
MIN	.063	.057	.063	.058	.061
MAX	.067	.081	.067	.062	.063
MEAN	.065	.061	.065	.061	.063
STDEV	.001	.006	.001	.001	.001
"JAMES 2"					
	.100	.081	.082	.081	.071
	.102	.079	.082	.081	.069
	.100	.081	.084	.081	.071
	.106	.081	.094	.079	.077
	.108	.077	.082	.079	.071
	.106	.083	.082	.077	.071
	.108	.081	.083	.111	.069
	.108	.079	.084	.081	.073
	.108	.079	.082	.081	.069
	.110	.081	.086	.081	.087
	.106	.079	.080	.079	.077
	.108	.081	.080	.081	.071
	.108	.081	.086	.081	.069
MIN	.100	.077	.080	.077	.069
MAX	.110	.083	.094	.111	.087
MEAN	.106	.080	.084	.083	.073
STDEV	.003	.002	.004	.009	.005

TABLE A.9 (continued)

TOTAL PHOSPHORUS DATA FOR FREEZING STUDY
(concentration in mg/l)

STATION	DAY ZERO	DAY ONE	HOLDING TIME	FROZEN 7 DAYS	FROZEN 28 DAYS
'YORK 1'					
	.026	.026	.026	.041	.030
	.026	.026	.026	.033	.030
	.026	.026	.028	.035	.034
	.026	.028	.026	.035	.030
	.031	.026	.028	.035	.032
	.029	.026	.028	.035	.032
	.029	.026	.028	.037	.030
	.031	.028	.026	.037	.040
	.029	.028	.028	.033	.032
	.031	.026	.028	.035	.032
	.029	.036	.028	.035	.032
	.029	.028	.028	.035	.032
	.029	.028	.028	.035	.032
MIN	.026	.026	.026	.033	.030
MAX	.031	.036	.028	.041	.040
MEAN	.029	.028	.027	.035	.032
STDEV	.002	.003	.001	.002	.003
'YORK 2'					
	.133	.132	.135	.128	.130
	.133	.130	.135	.134	.134
	.135	.132	.137	.136	.134
	.135	.141	.135	.134	.132
	.135	.130	.139	.136	.132
	.133	.132	.137	.136	.130
	.135	.132	.137	.132	.134
	.133	.135	.135	.134	.134
	.139	.132	.137	.134	.130
	.133	.132	.137	.136	.132
	.133	.132	.135	.136	.132
	.131	.132	.137	.134	.132
	.137	.132	.135	.134	.134
MIN	.131	.130	.135	.128	.130
MAX	.139	.141	.139	.136	.134
MEAN	.134	.133	.136	.134	.132
STDEV	.002	.003	.001	.002	.002

Appendix B

Graphical Summaries of Raw Data

Figures B1-B9	Mean Concentration vs. Treatment by Station/Salinity
Figures B10-B45	Concentration (mean, standard deviation, observations) vs Treatment

Figure B1. Comparison of mean nitrite concentrations by treatment, station and salinity

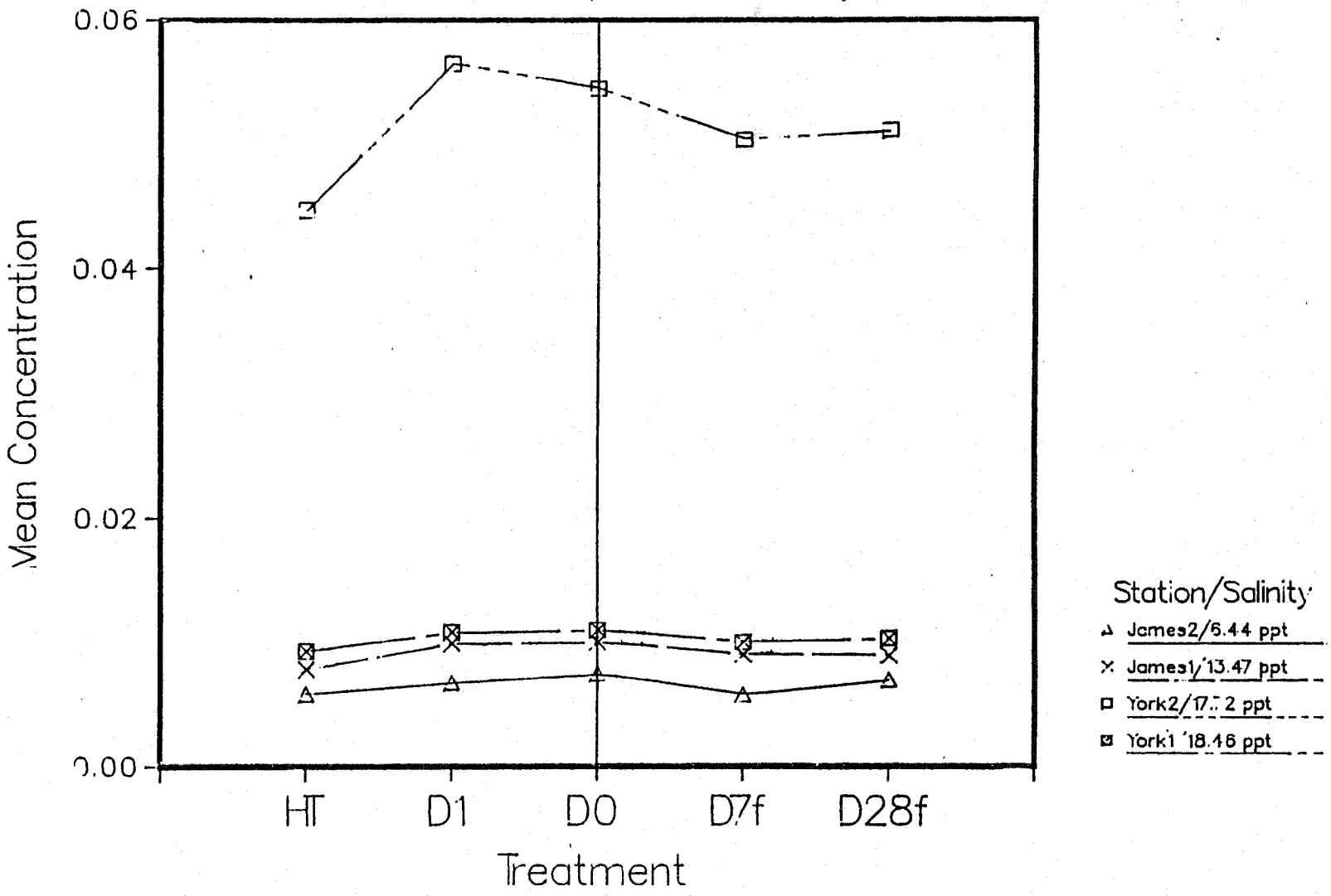


Figure B2. Comparison of mean nitrite+nitrate concentrations by treatment, station and salinity

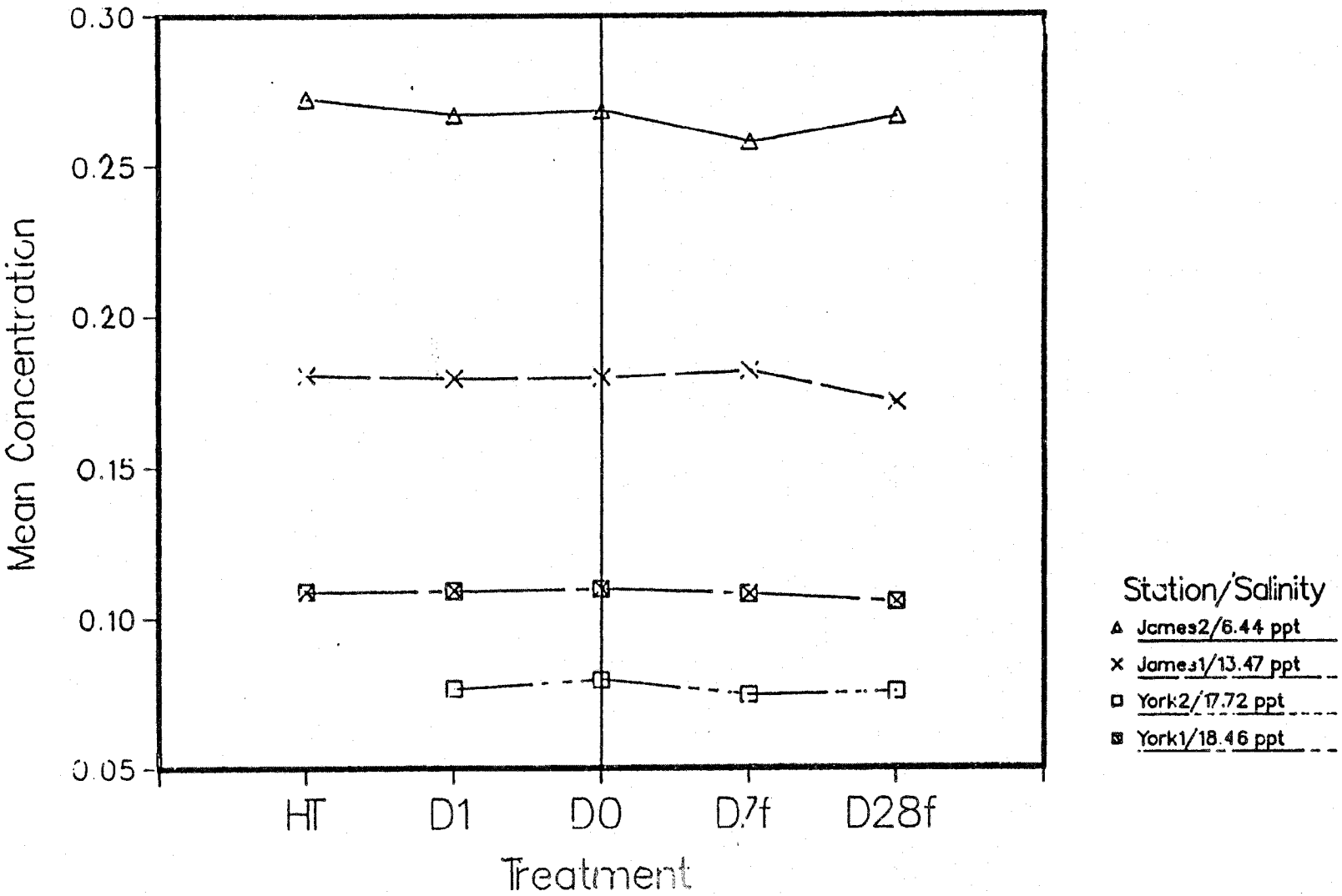


Figure B3. Comparison of mean ammonia concentrations by treatment, station and salinity

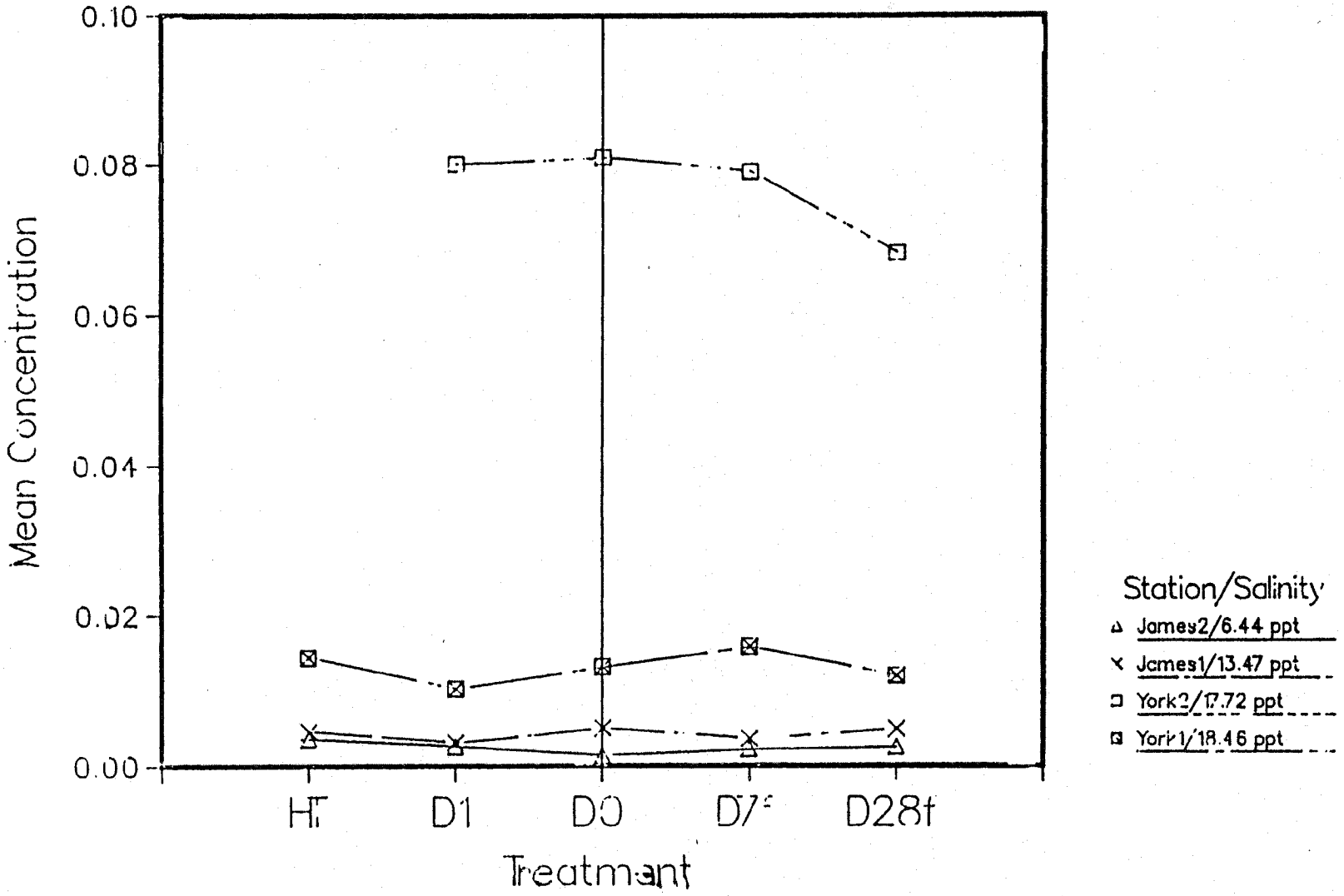


Figure B4. Comparison of mean total Kjeldahl N. concentrations by treatment, station and salinity

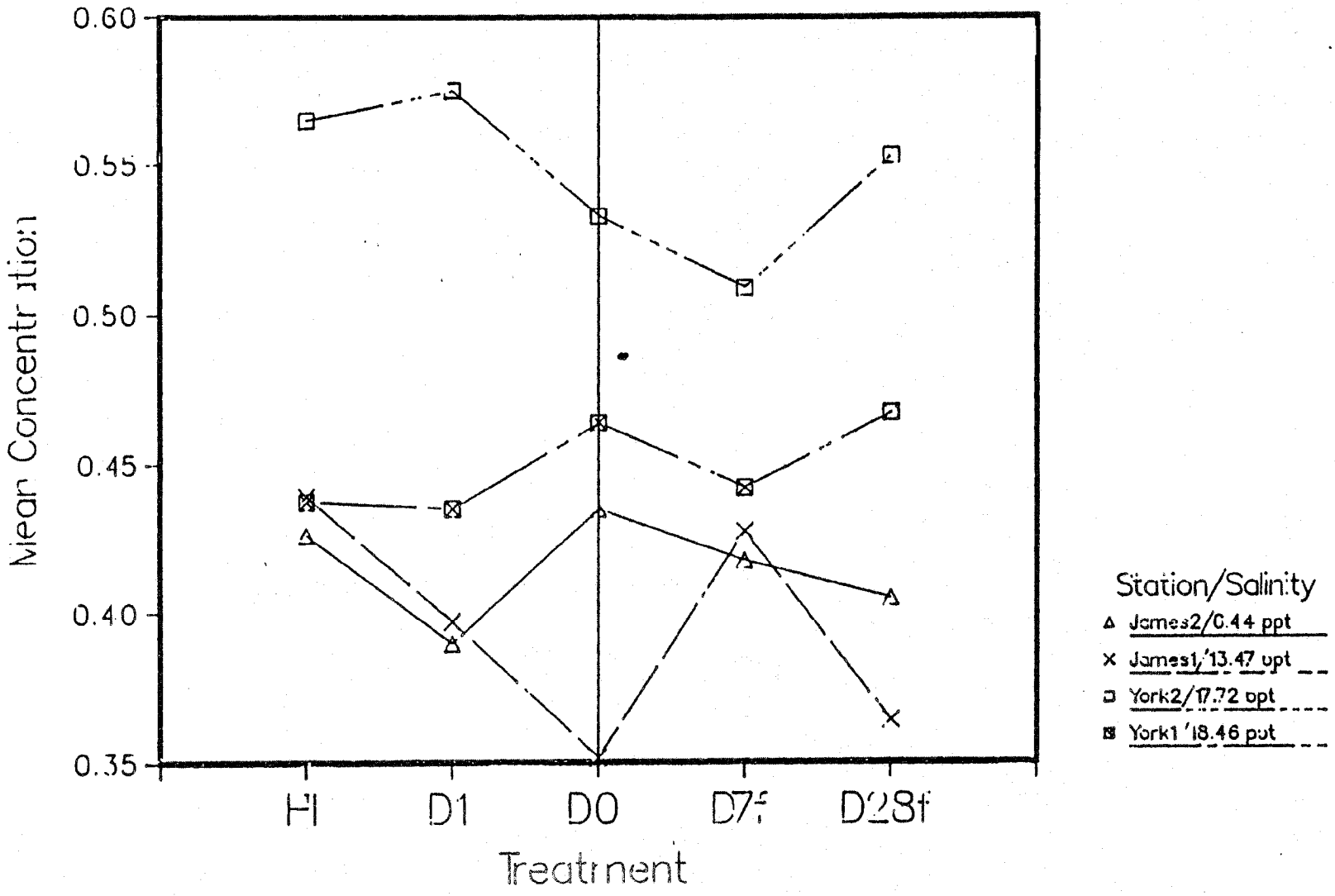


Figure B5. Comparison of mean orthophosphate concentrations by treatment, station and salinity

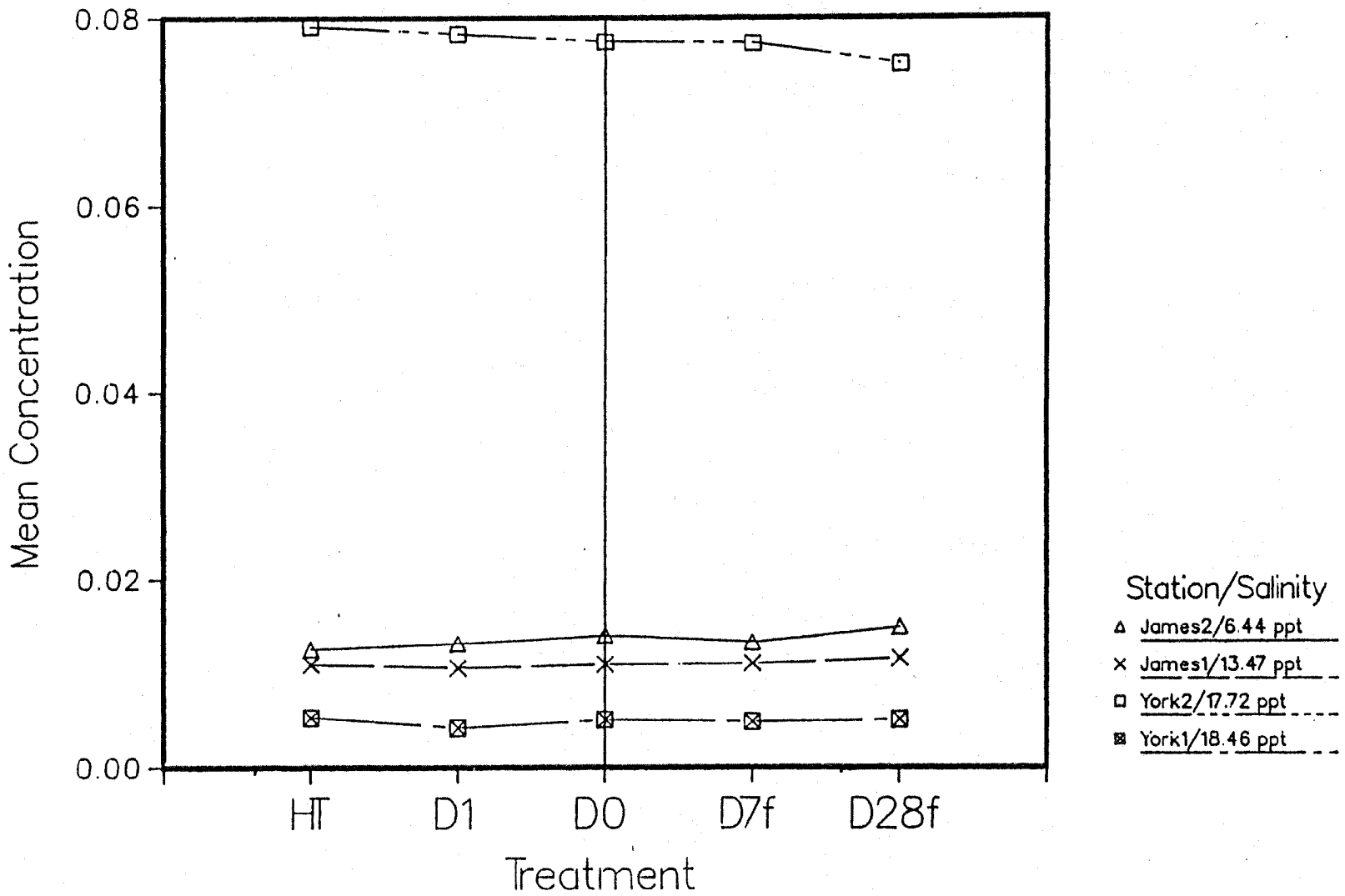


Figure B6. Comparison of mean total dissolved P. concentrations by treatment, station and salinity

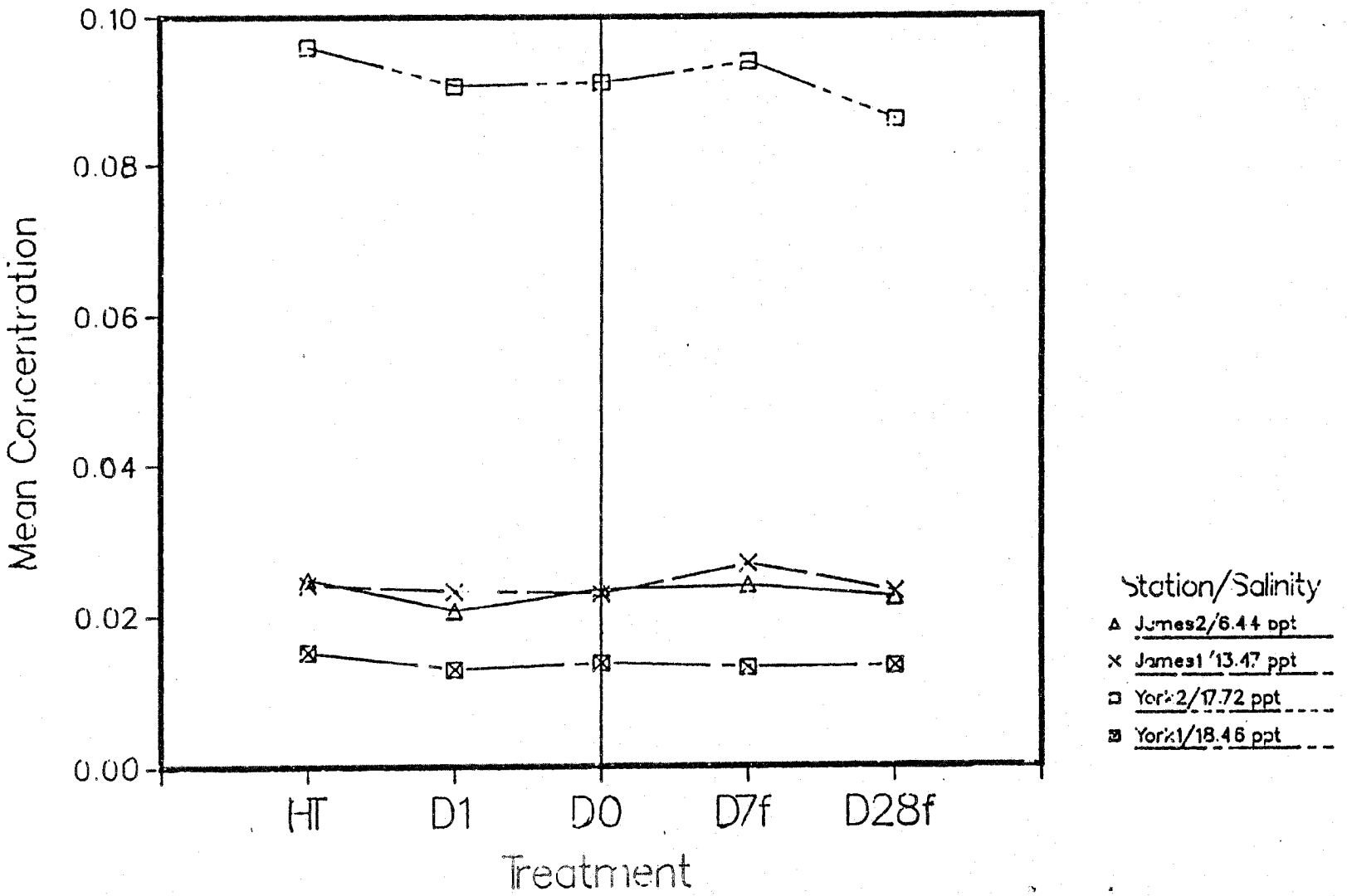


Figure B7. Comparison of mean total phosphorus concentrations by treatment, station and salinity

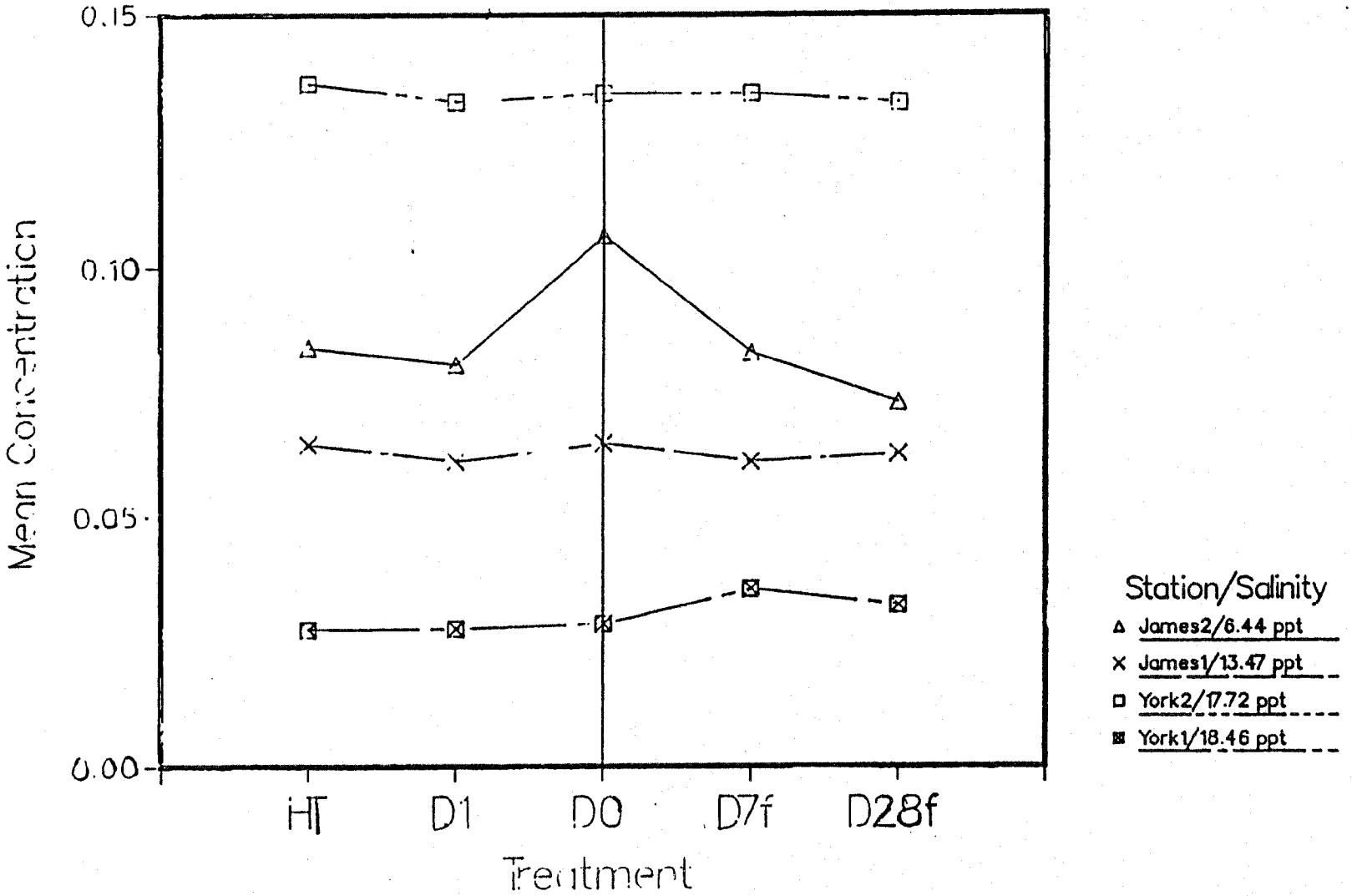


Figure B8. Comparison of mean suspended solids concentrations by treatment, station and salinity

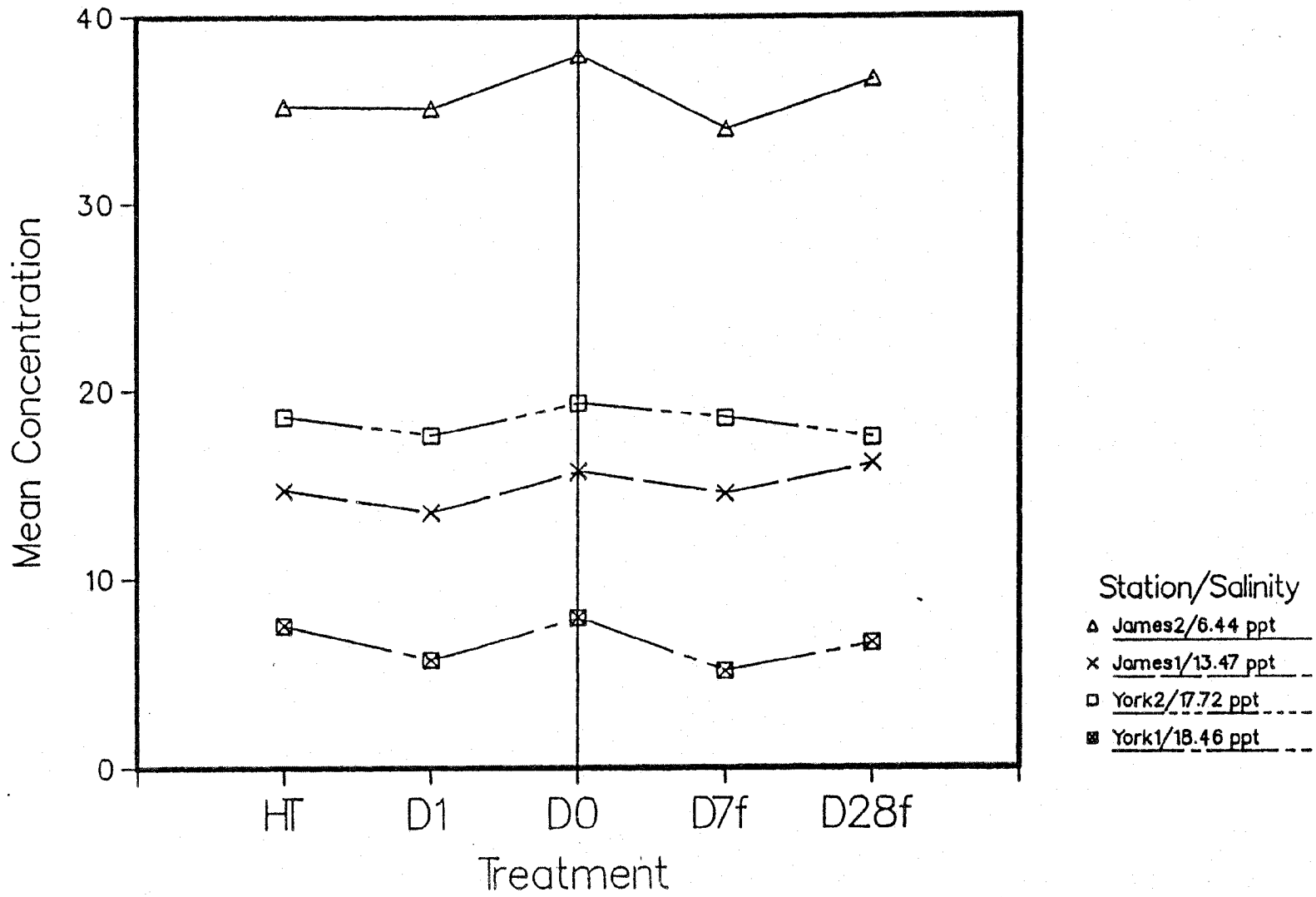


Figure B9. Comparison of mean silica concentrations by treatment, station and salinity

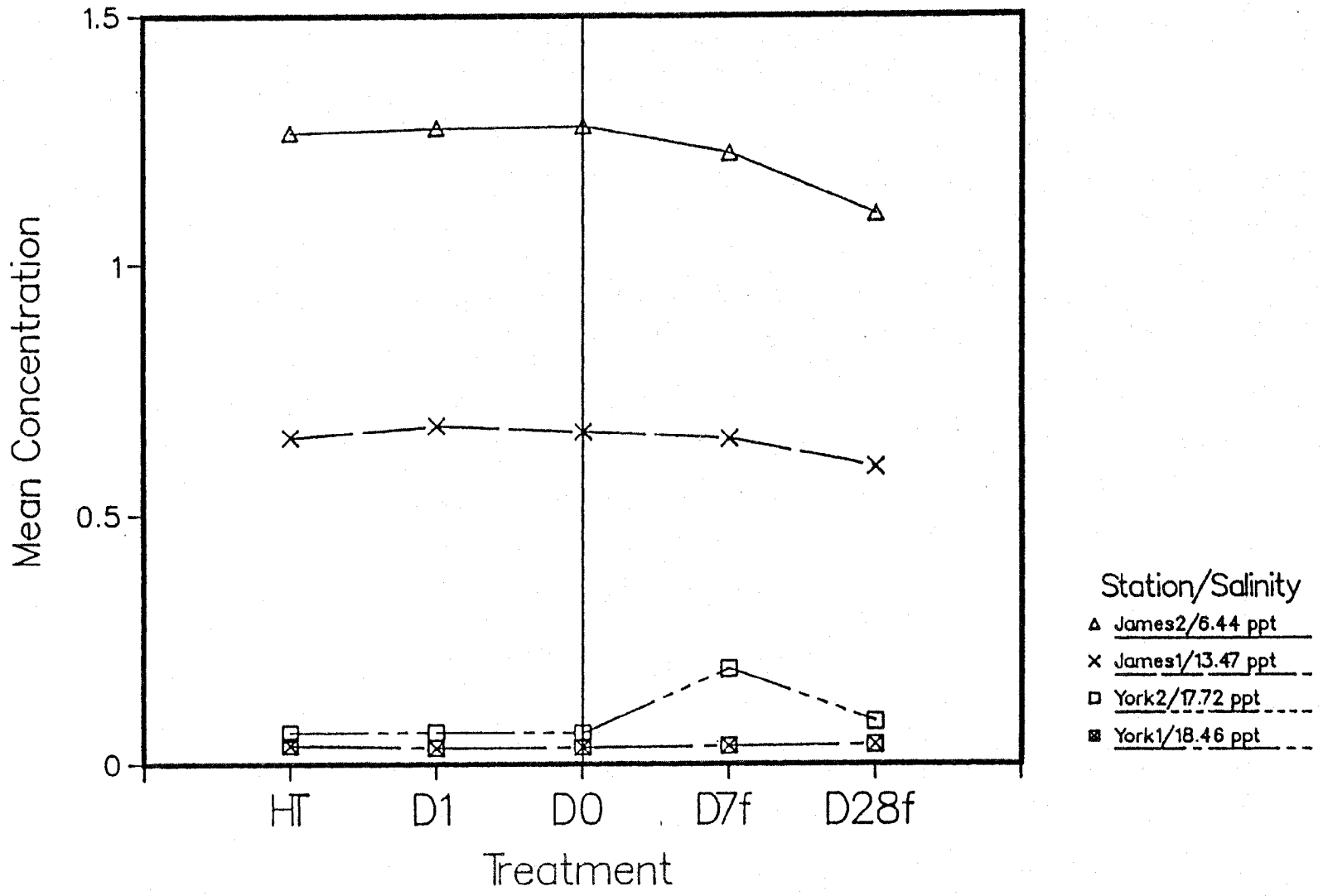
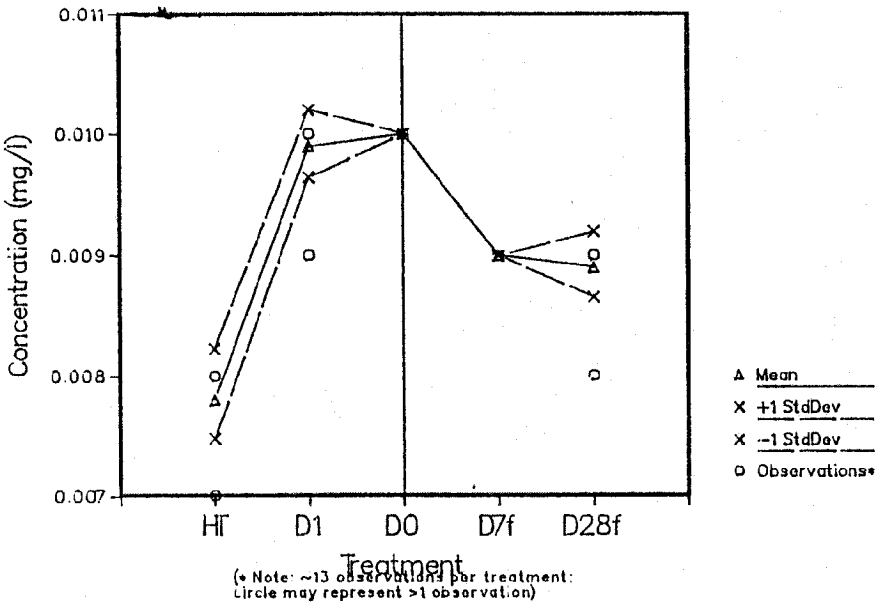
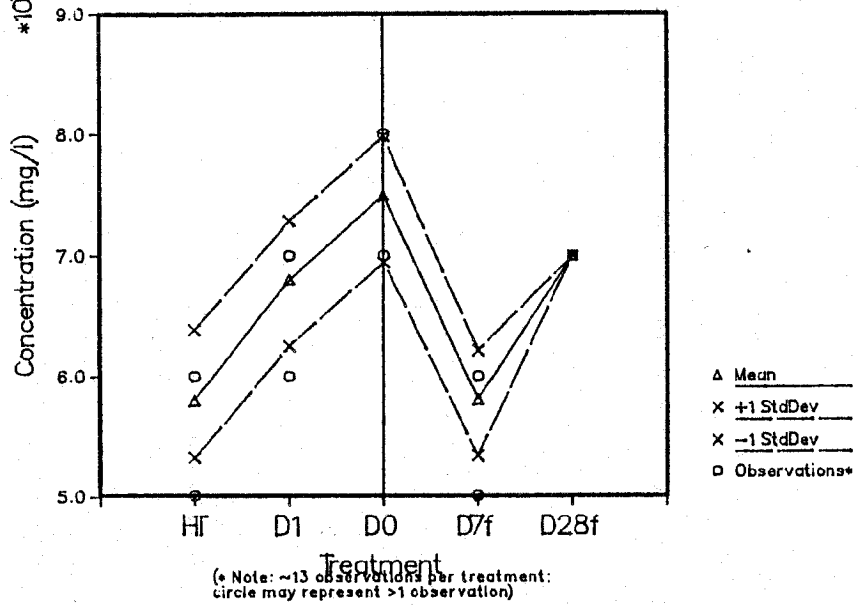


Figure B10. Comparison of nitrite concentrations by treatment at James 1



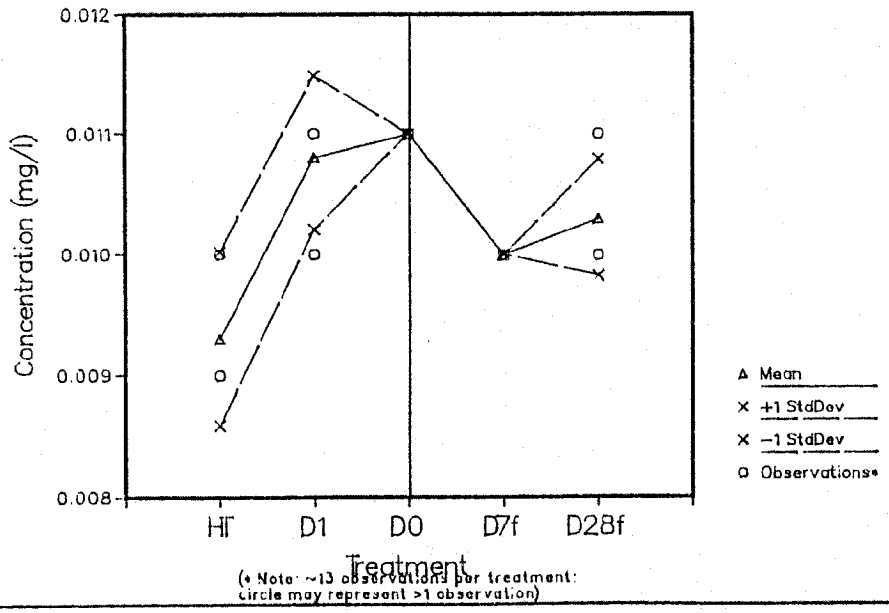
(* Note: ~13 observations per treatment: circle may represent >1 observation)

Figure B11. Comparison of nitrite concentrations by treatment at James 2



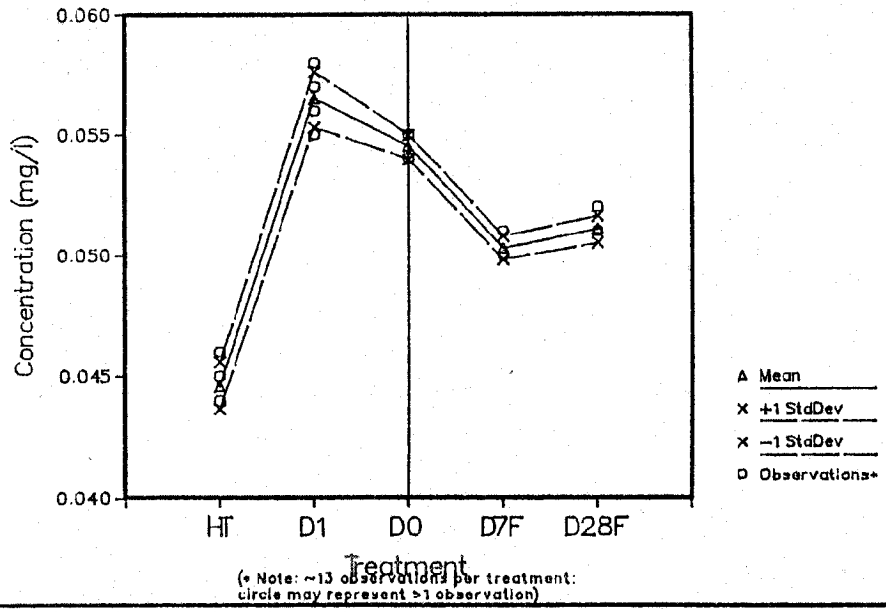
(* Note: ~13 observations per treatment: circle may represent >1 observation)

Figure B12. Comparison of nitrite concentrations by treatment at York 1



(* Note: ~13 observations per treatment: circle may represent >1 observation)

Figure B13. Comparison of nitrite concentrations by treatment at York 2



(* Note: ~13 observations per treatment: circle may represent >1 observation)

Figure B14. Comparison of nitrite+nitrate concentrations by treatment at James 1

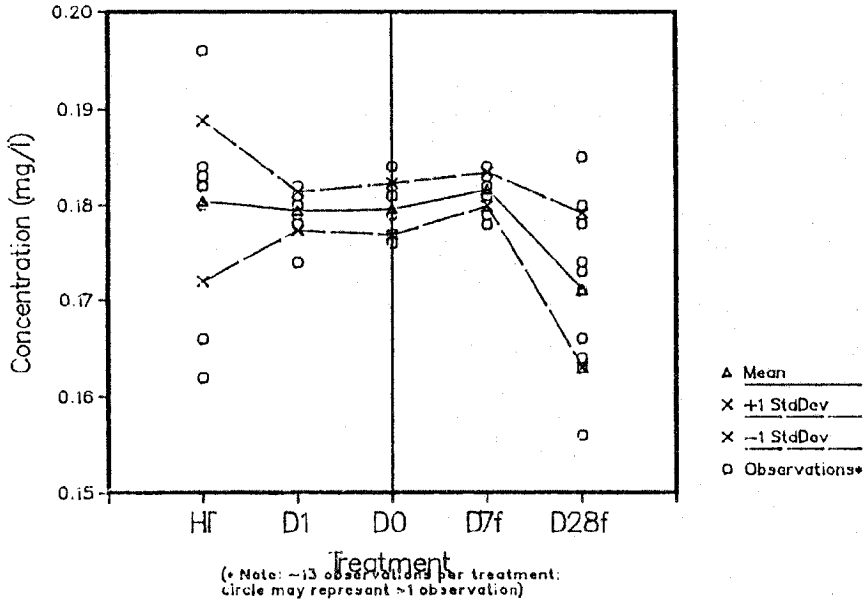


Figure B15. Comparison of nitrite+nitrate concentrations by treatment at James 2

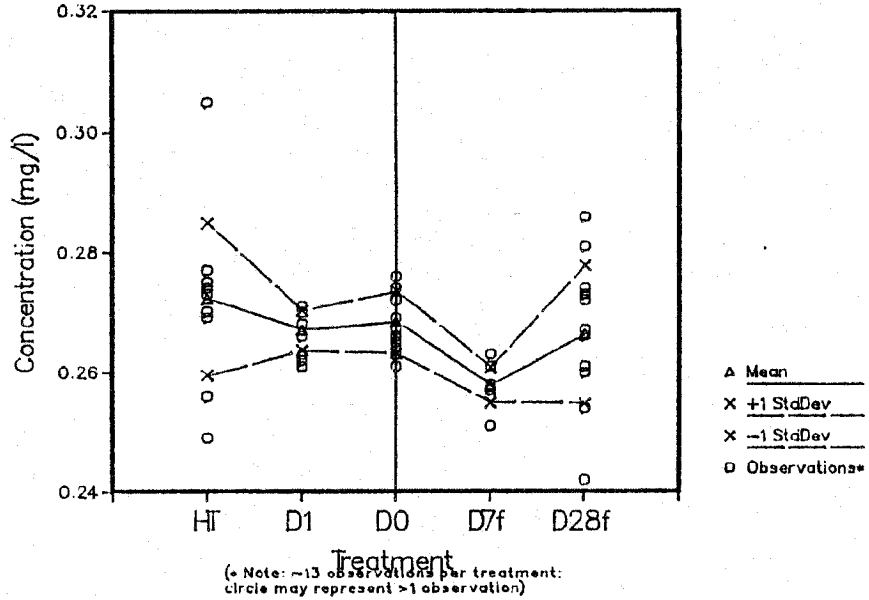


Figure B16. Comparison of nitrite+nitrate concentrations by treatment at York 1

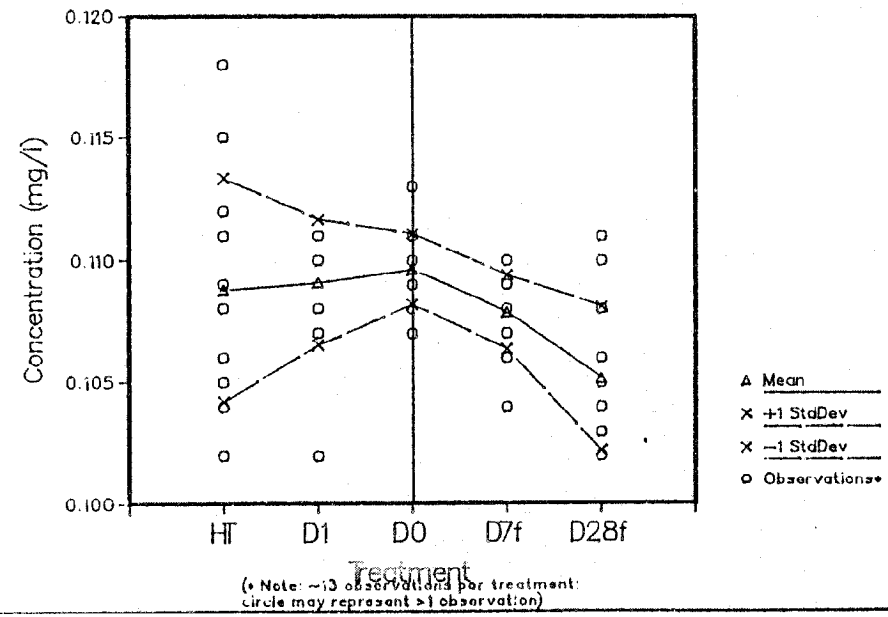


Figure B17. Comparison of nitrite+nitrate concentrations by treatment at York 2

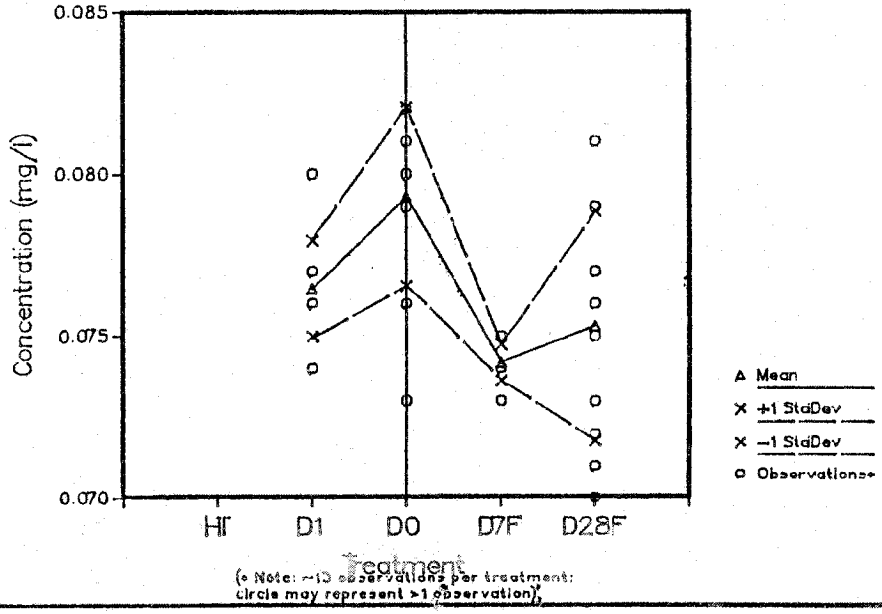
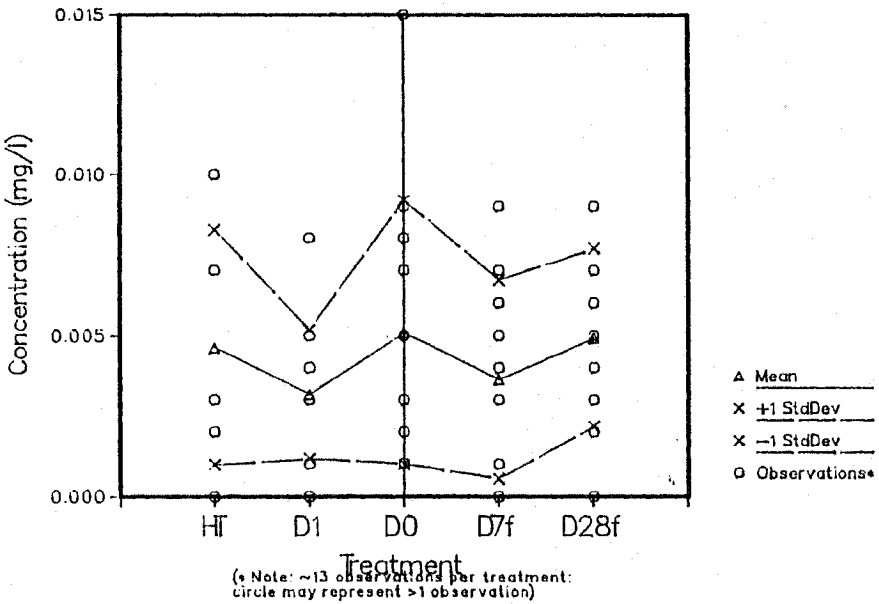
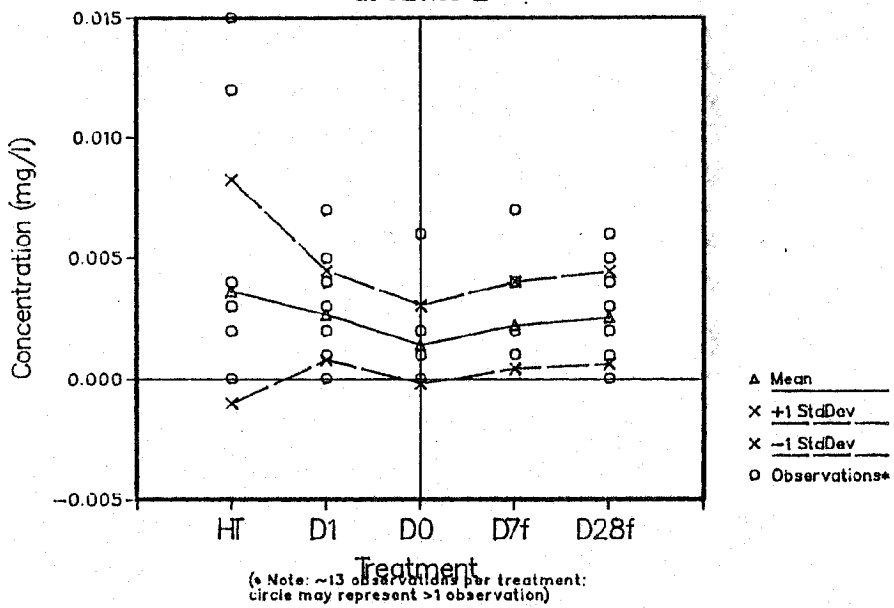


Figure B18. Comparison of ammonia concentrations by treatment at James 1



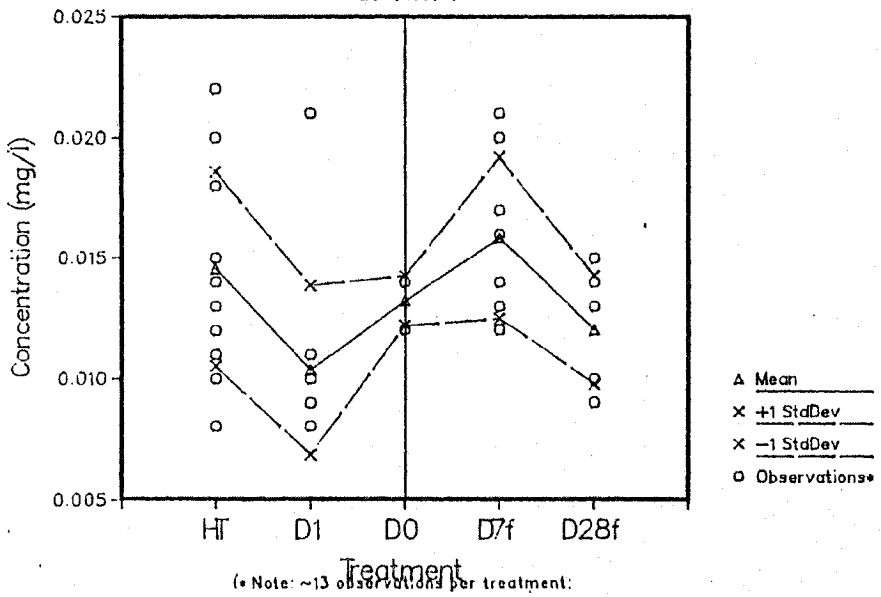
(* Note: ~13 observations per treatment: circle may represent >1 observation)

Figure B19. Comparison of ammonia concentrations by treatment at James 2



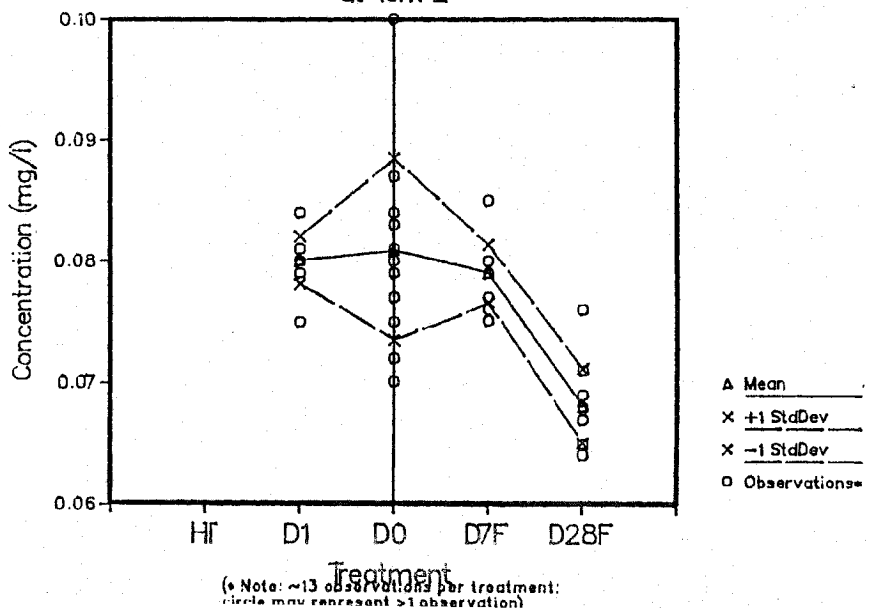
(* Note: ~13 observations per treatment: circle may represent >1 observation)

Figure B20. Comparison of ammonia concentrations by treatment at York 1



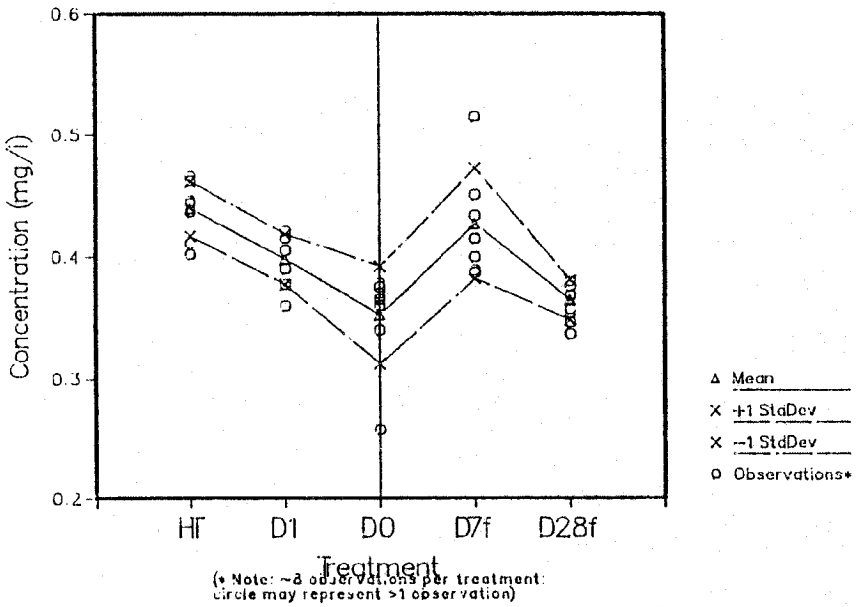
(* Note: ~13 observations per treatment:

Figure B21. Comparison of ammonia concentrations by treatment at York 2



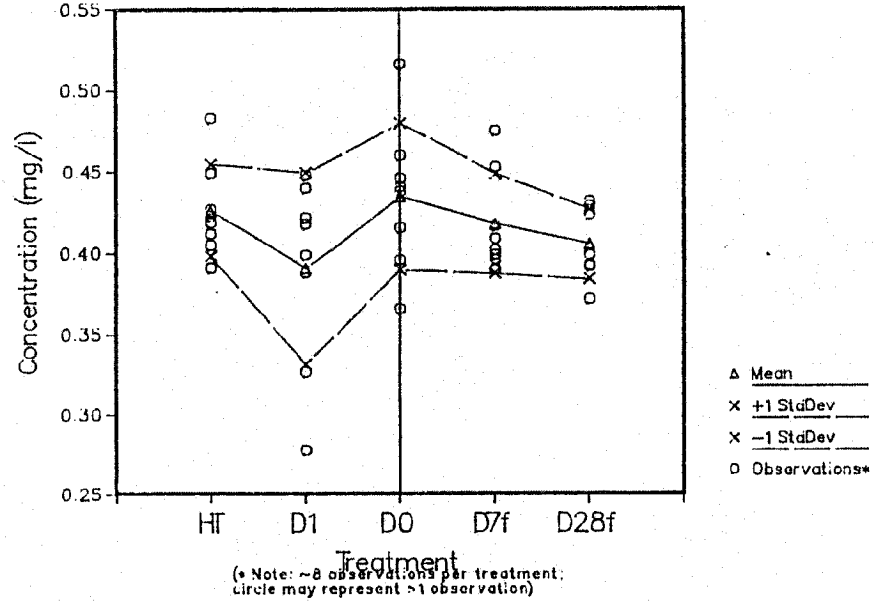
(* Note: ~13 observations per treatment: circle may represent >1 observation)

Figure B22. Comparison of total Kjeldahl N. concentrations by treatment at James 1



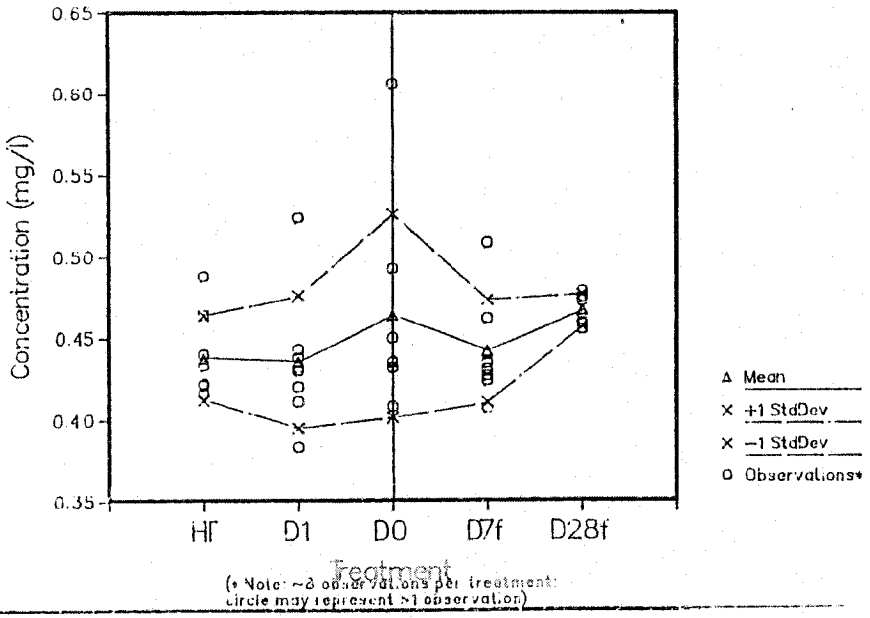
(* Note: ~8 observations per treatment; circle may represent >1 observation)

Figure B23. Comparison of total Kjeldahl N. concentrations by treatment at James 2



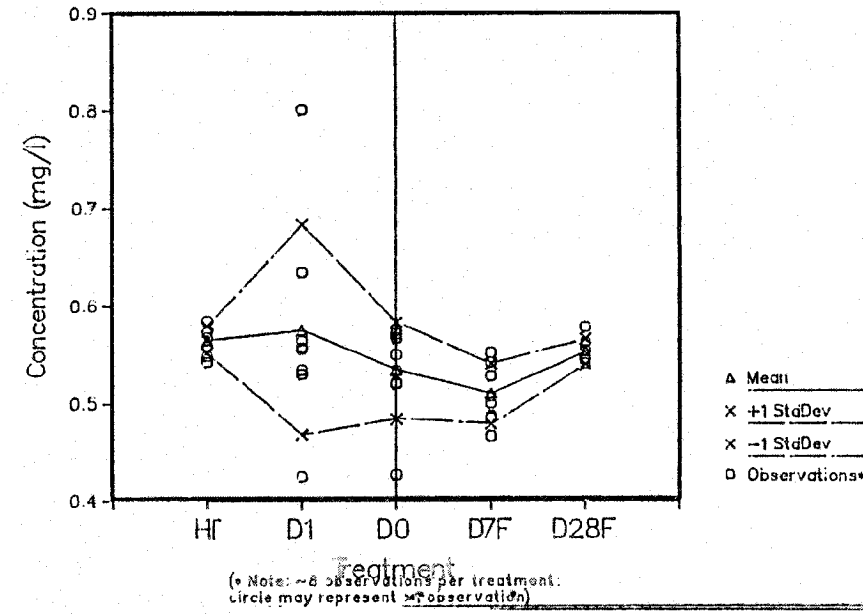
(* Note: ~8 observations per treatment; circle may represent >1 observation)

Figure B24. Comparison of total Kjeldahl N. concentrations by treatment at York 1



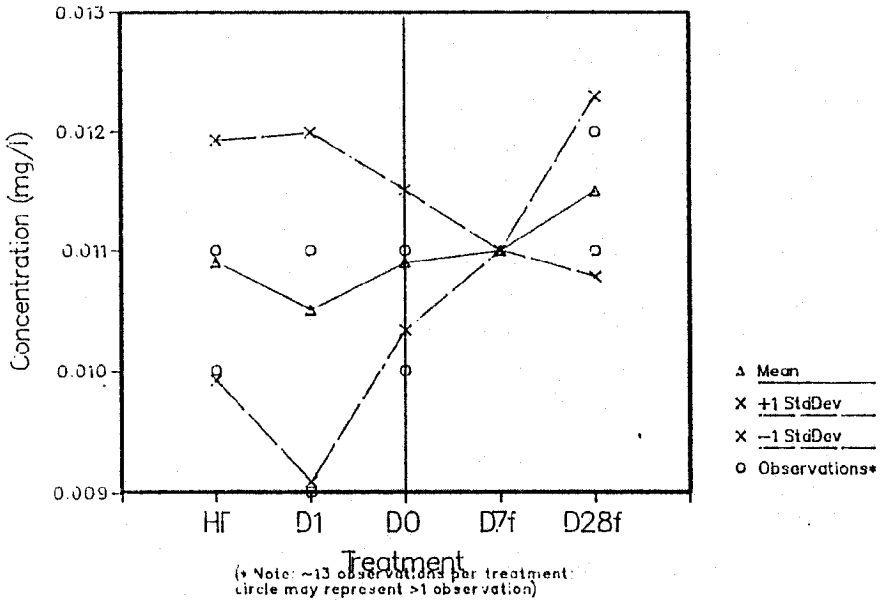
(* Note: ~8 observations per treatment; circle may represent >1 observation)

Figure B25. Comparison of total Kjeldahl N. concentrations by treatment at York 2



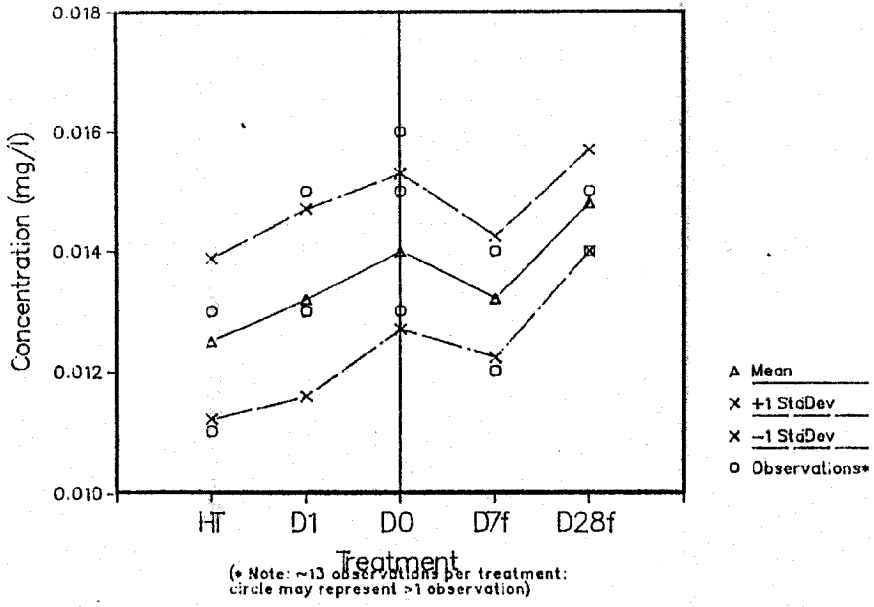
(* Note: ~8 observations per treatment; circle may represent >1 observation)

Figure B26. Comparison of orthophosphate concentrations by treatment at James 1



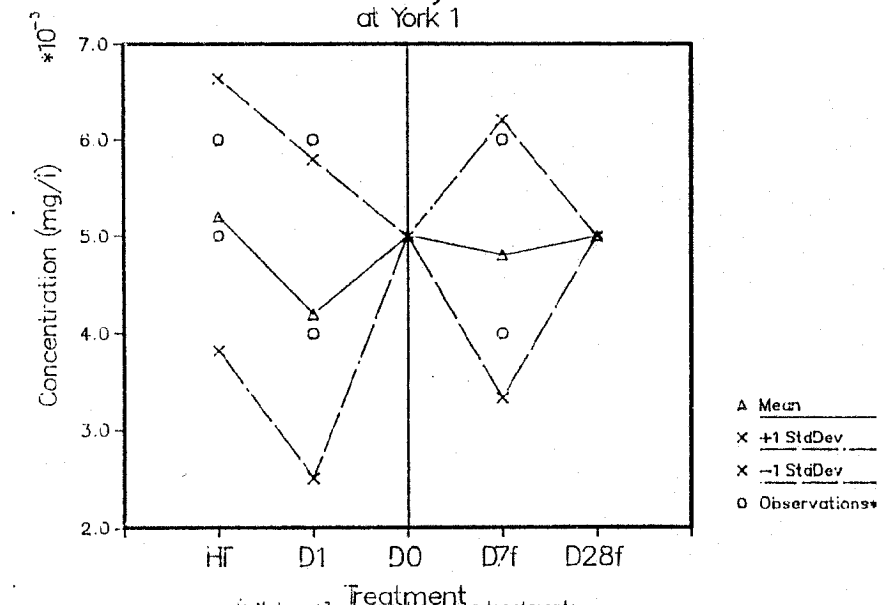
(* Note: ~13 observations per treatment: circle may represent >1 observation)

Figure B27. Comparison of orthophosphate concentrations by treatment at James 2



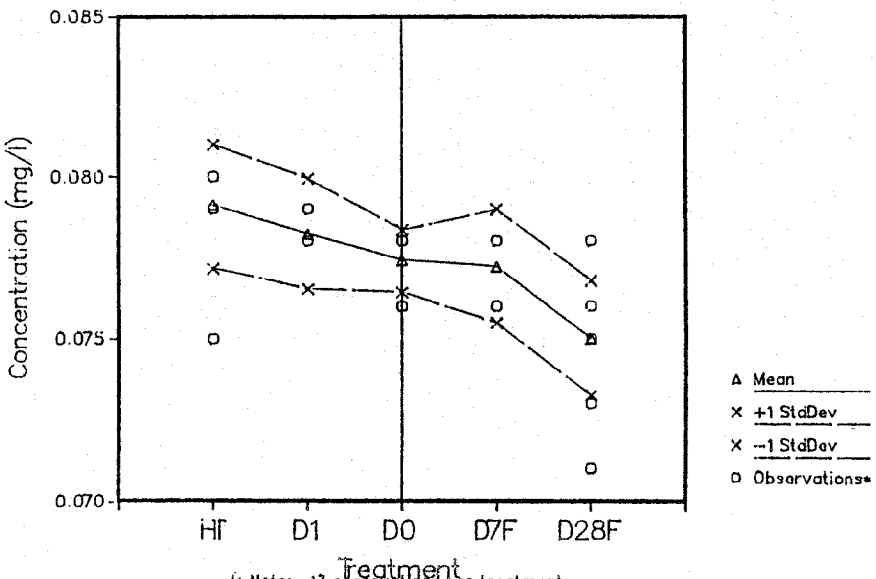
(* Note: ~13 observations per treatment: circle may represent >1 observation)

Figure B28. Comparison of orthophosphate concentrations by treatment at York 1



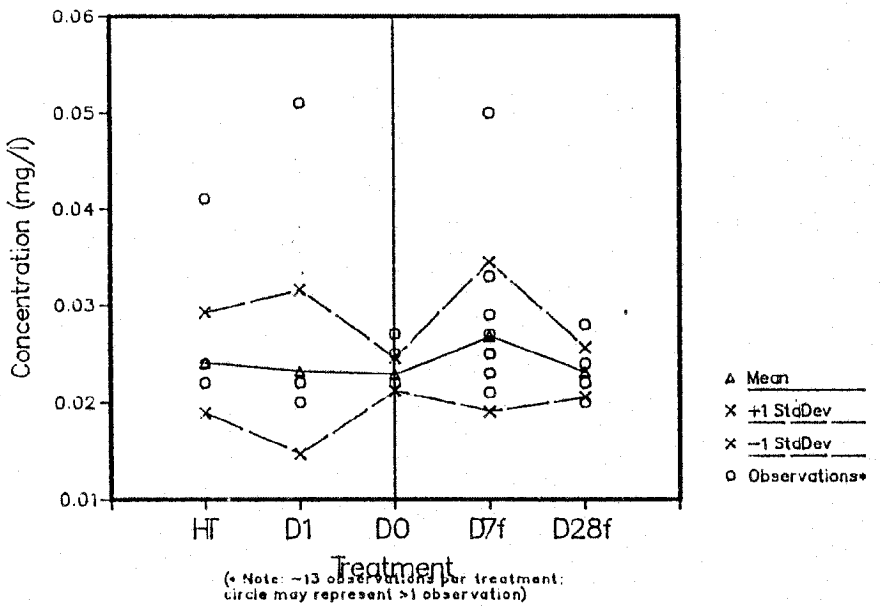
(* Note: ~13 observations per treatment: circle may represent >1 observation)

Figure B29. Comparison of orthophosphate concentrations by treatment at York 2



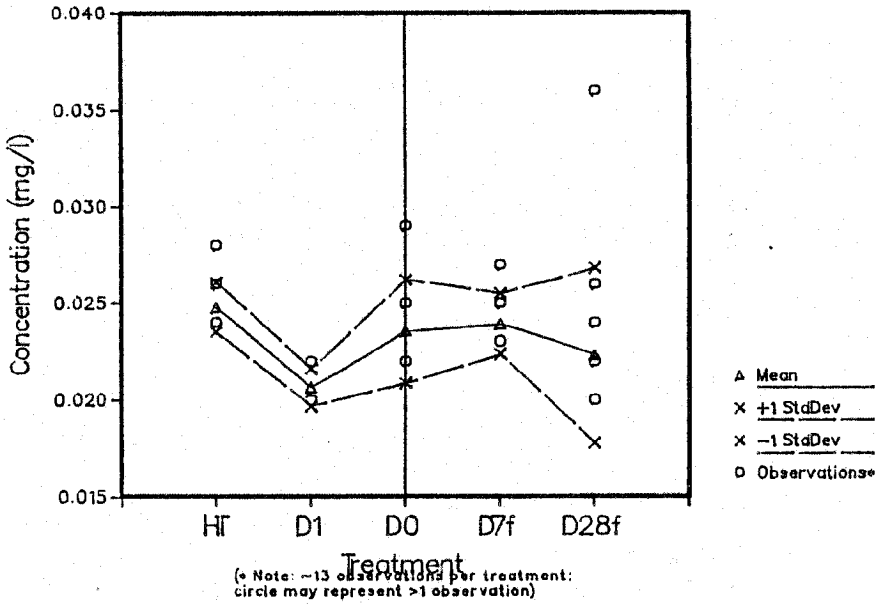
(* Note: ~13 observations per treatment: circle may represent >1 observation)

Figure B30. Comparison of total dissolved P. concentrations by treatment at James 1



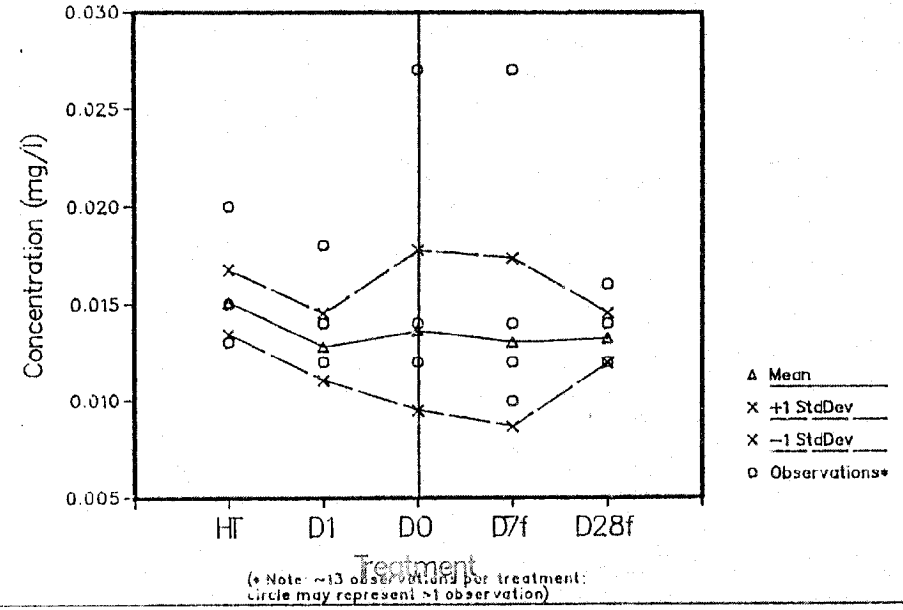
(* Note: ~13 observations per treatment; circle may represent >1 observation)

Figure B31. Comparison of total dissolved P. concentrations by treatment at James 2



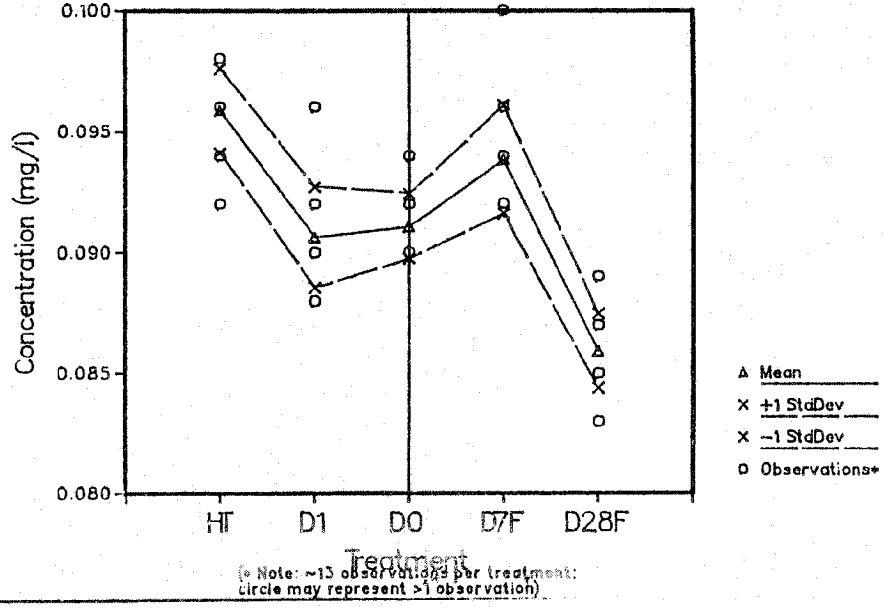
(* Note: ~13 observations per treatment; circle may represent >1 observation)

Figure B32. Comparison of total dissolved P. concentrations by treatment at York 1



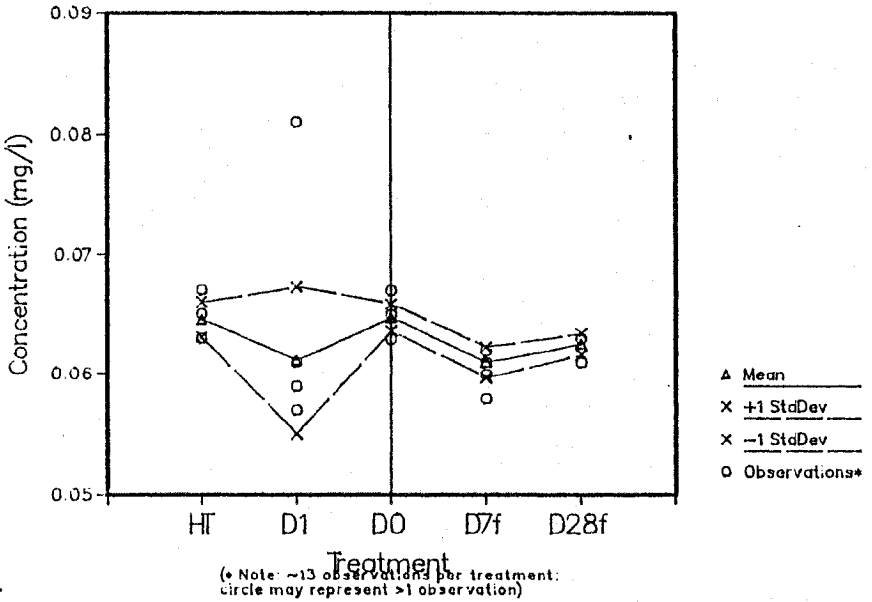
(* Note: ~13 observations per treatment; circle may represent >1 observation)

Figure B33. Comparison of total dissolved P. concentrations by treatment at York 2



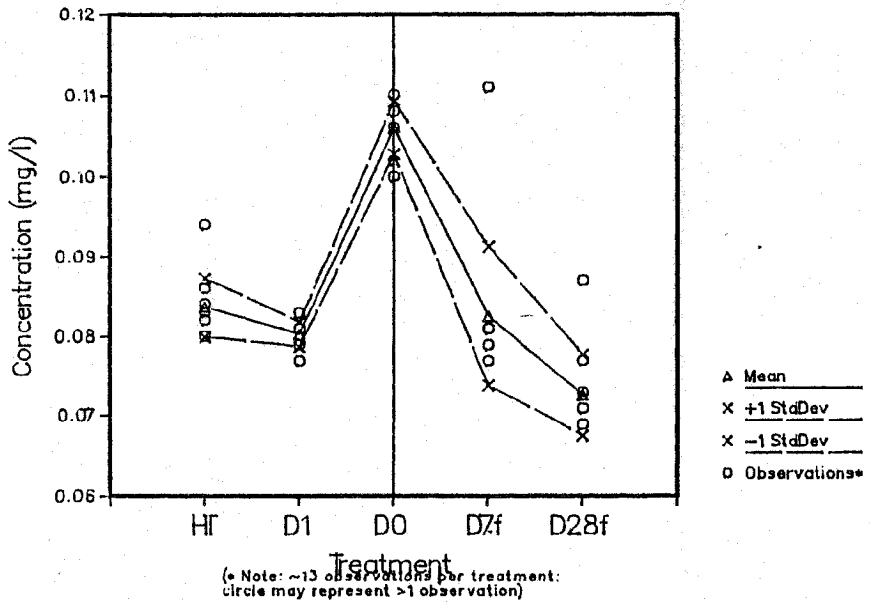
(* Note: ~13 observations per treatment; circle may represent >1 observation)

Figure B34. Comparison of total phosphorus concentrations by treatment at James 1



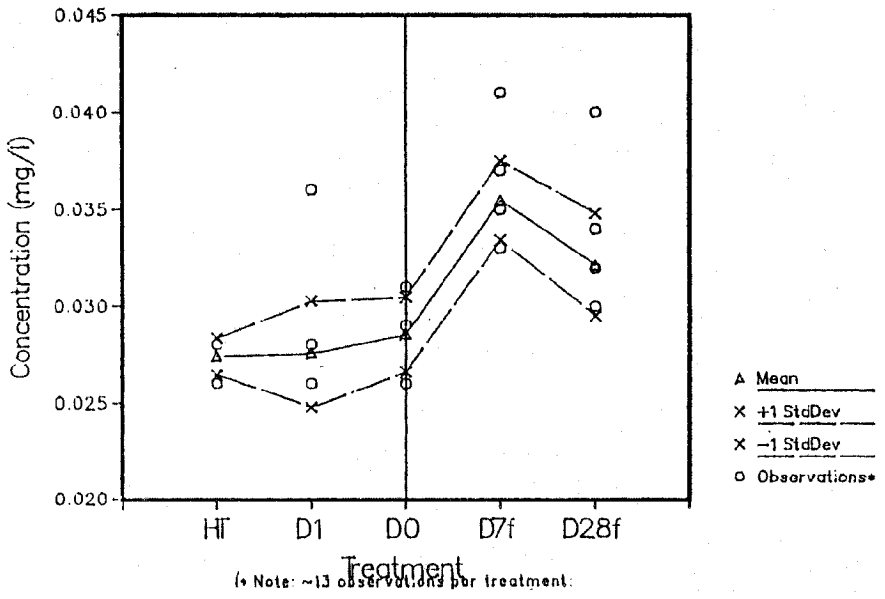
(* Note: ~13 observations per treatment; circle may represent >1 observation)

Figure B35. Comparison of total phosphorus concentrations by treatment at James 2



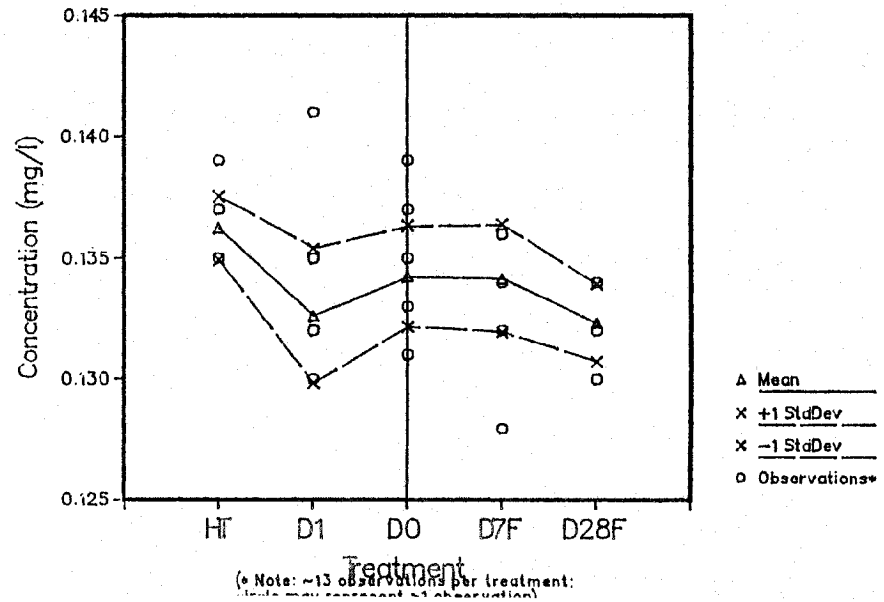
(* Note: ~13 observations per treatment; circle may represent >1 observation)

Figure B36. Comparison of total phosphorus concentrations by treatment at York 1



(* Note: ~13 observations per treatment;

Figure B37. Comparison of total phosphorus concentrations by treatment at York 2



(* Note: ~13 observations per treatment;

Figure B38. Comparison of suspended solids concentrations by treatment at James 1

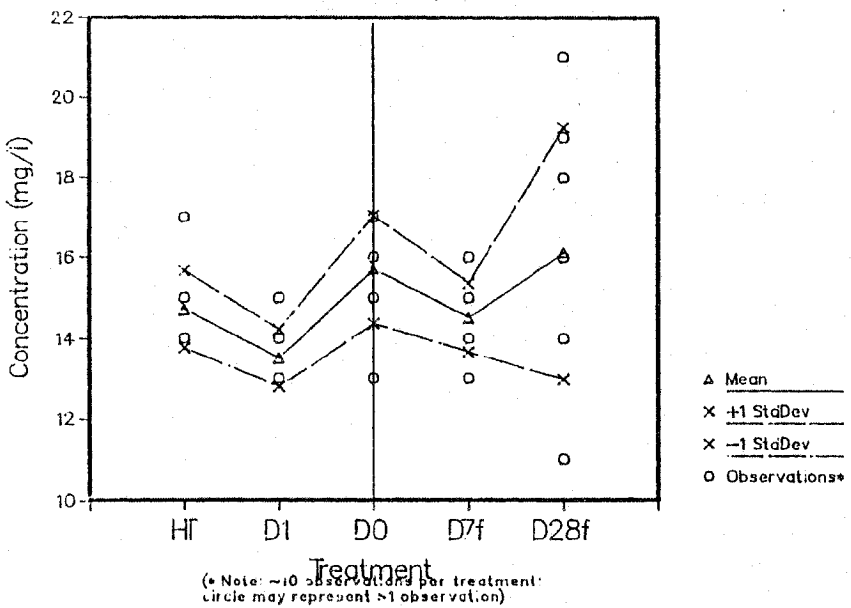


Figure B39. Comparison of suspended solids concentrations by treatment at James 2

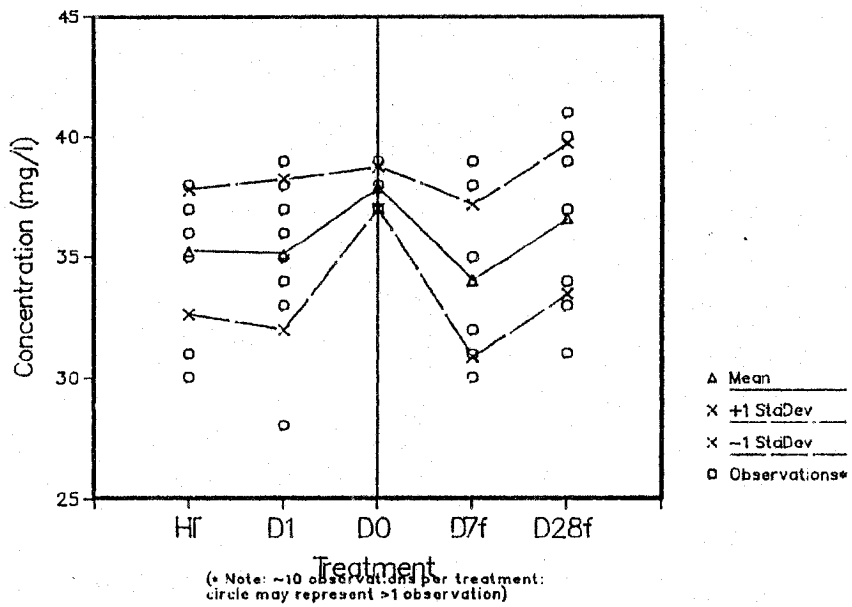


Figure B40. Comparison of suspended solids concentrations by treatment at York 1

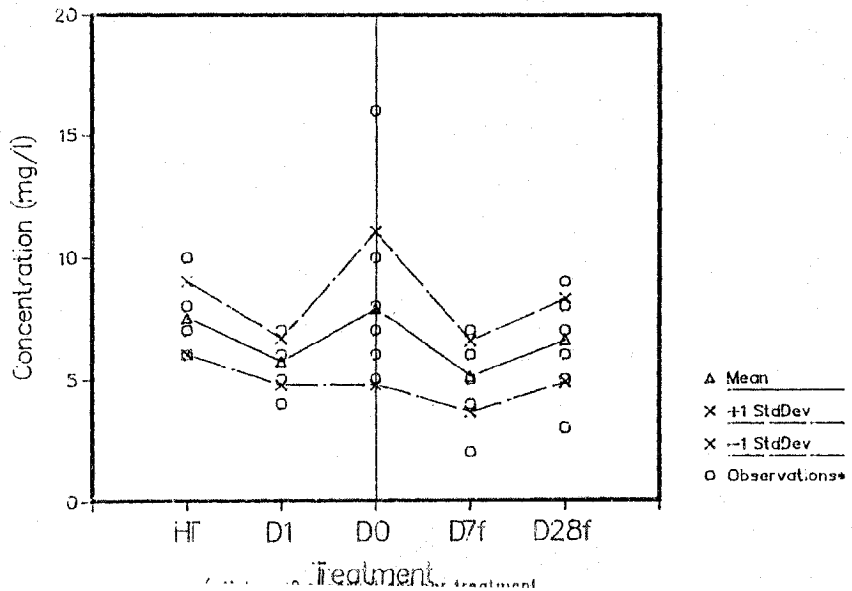


Figure B41. Comparison of suspended solids concentrations by treatment at York 2

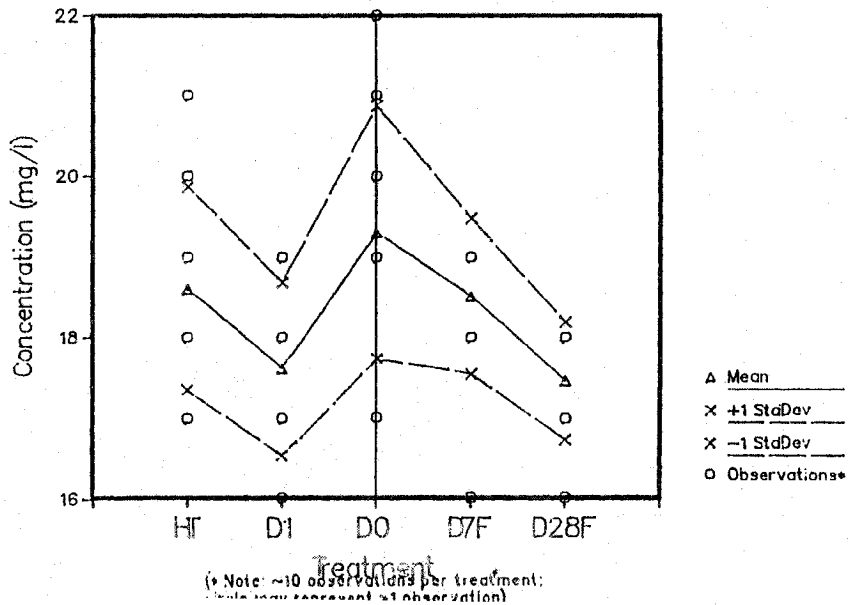
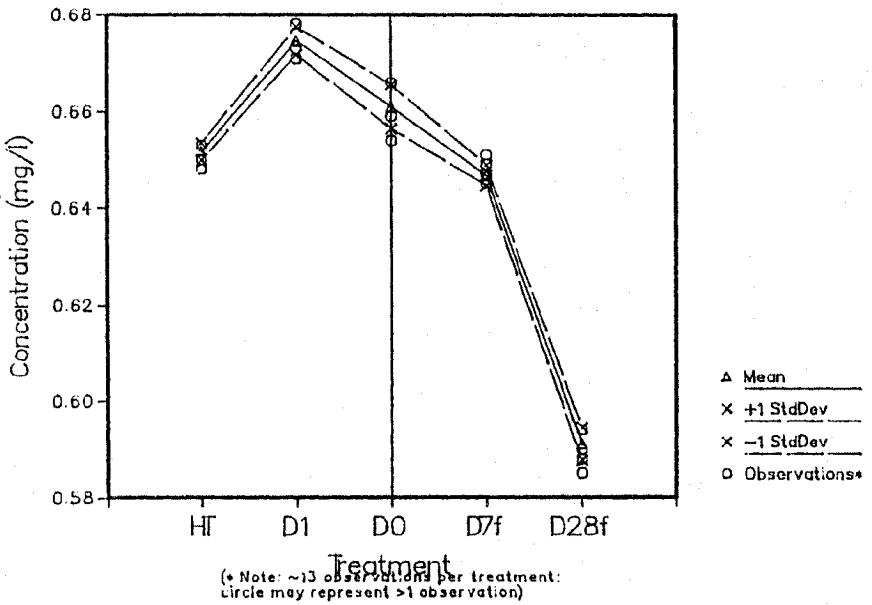
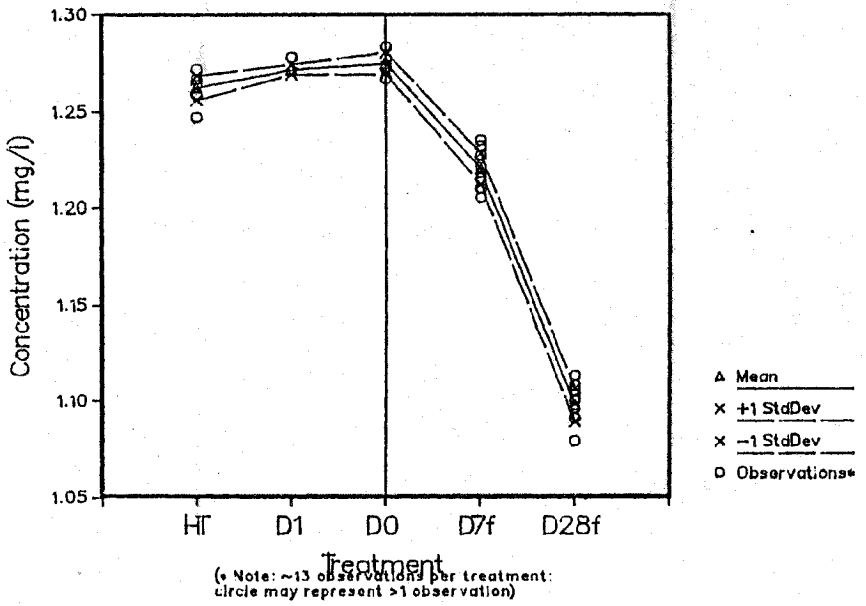


Figure B42. Comparison of silica concentrations by treatment at James 1



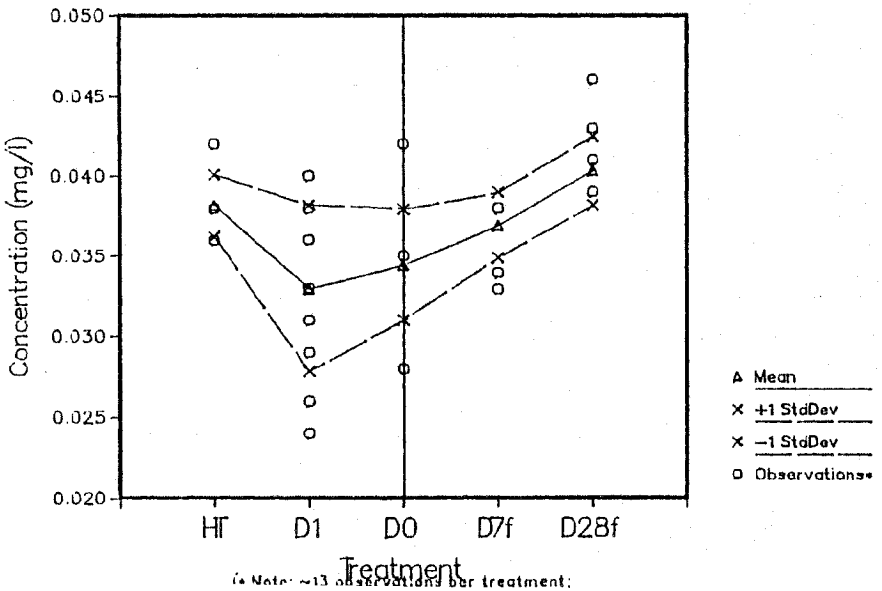
(* Note: ~13 observations per treatment; circle may represent >1 observation)

Figure B43. Comparison of silica concentrations by treatment at James 2



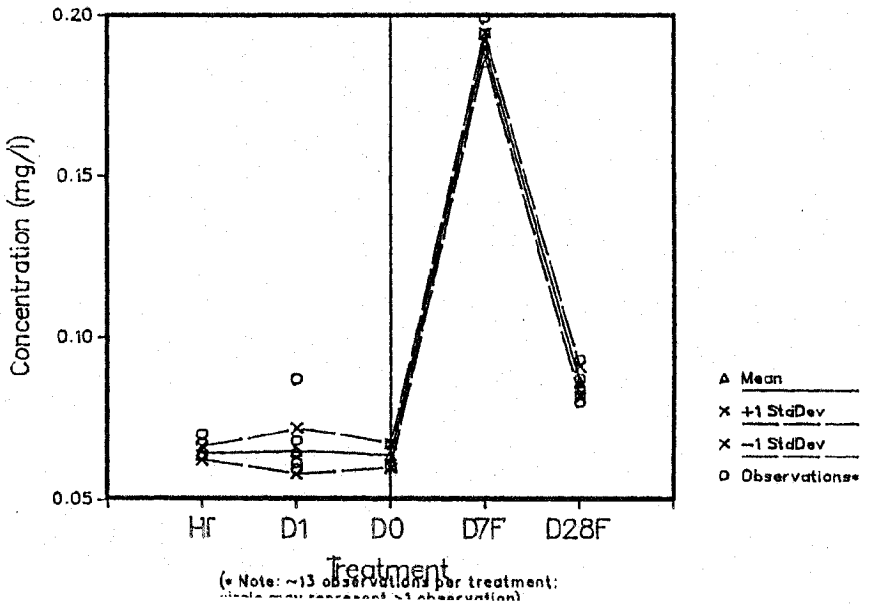
(* Note: ~13 observations per treatment; circle may represent >1 observation)

Figure B44. Comparison of silica concentrations by treatment at York 1



(* Note: ~13 observations per treatment;

Figure B45. Comparison of silica concentrations by treatment at York 2



(* Note: ~13 observations per treatment;

Appendix C

Results of Statistical Analyses

CONTENTS:

Abbreviations used:

NO2	Nitrite-Nitrogen
NO23	Nitrate-Nitrite-Nitrogen
NH3	Ammonia Nitrogen
TKN	Total Kjeldahl Nitrogen
OP	Orthophosphate
TP	Total Phosphorus
TDP	Total Dissolved Phosphorus
SS	Suspended Solids
SI	Silica

D0	Day 0 treatment (control)
D1	Day 1 treatment
HT	Holding Time treatment
D7f or D7frz	Day 7 (frozen) treatment
D28f or D28frz	Day 28 (frozen) treatment

Table C1. Paired t-test
Null hypothesis: Control (Day 0) mean equals treatment mean.

ANALYSIS	TREATMENT	STATION James 1	James 2	York 1	York 2
OP	Day 1	NS	.020	---	.014
	Hold time	NS	.002	---	.005
	Day 7-frz	---	NS	---	NS
	Day 28-frz	NS	.014	---	<.001
TDP	Day 1	NS	.003	NS	NS
	Hold time	NS	NS	NS	<.001
	Day 7-frz	NS	NS	NS	<.001
	Day 28-frz	NS	NS	NS	<.001
TP	Day 1	NS	<.001	NS	NS
	Hold time	NS	<.001	.033	.009
	Day 7-frz	<.001	<.001	<.001	NS
	Day 28-frz	<.001	<.001	<.001	.023
NO2	Day 1	---	.002	---	<.001
	Hold time	---	<.001	---	<.001
	Day 7-frz	---	<.001	---	---
	Day 28-frz	---	---	---	<.001
NO23	Day 1	NS	NS	NS	.001
	Hold time	NS	NS	NS	(m)
	Day 7-frz	.025	<.001	.005	<.001
	Day 28-frz	.003	NS	<.001	.002
NH3	Day 1	NS	NS	.035	NS
	Hold time	NS	NS	NS	(m)
	Day 7-frz	NS	NS	.022	NS
	Day 28-frz	NS	NS	NS	<.001
TKN	Day 1	.005	.046	NS	NS
	Hold time	.001	NS	NS	NS
	Day 7-frz	.020	NS	NS	NS
	Day 28-frz	NS	NS	NS	NS
Silica	Day 1	<.001	NS	NS	NS
	Hold time	<.001	<.001	.008	NS
	Day 7-frz	<.001	<.001	.018	<.001
	Day 28-frz	<.001	<.001	<.001	<.001
SS	Day 1	.002	.021	NS	NS
	Hold time	NS	.006	NS	NS
	Day 7-frz	NS	.006	NS	NS
	Day 28-frz	NS	NS	NS	.018

Probability of getting test statistic (t) at least as large as that calculated if null hypothesis is true is shown.
NS = no significant difference between means (alpha=0.05)
--- = no variance in data group
(m) = missing data group

Table C2. Parametric Oneway Analysis of Variance

Null hypothesis: Treatment means are equal.

ANALYSIS	STATION James 1	James 2	York 1	York 2
NO2	<.0001	<.0001	<.0001	<.0001
NO23	.0001	.0011	.0015	<.0001
NH3	NS	NS	.0003	<.0001
TKN	<.0001	NS	NS	NS
OP	.0001	<.0001	.0001	<.0001
TDP	NS	.0012	NS	<.0001
TP	.002	<.0001	<.0001	.0001
SS	.0078	.0259	.0091	.0057
SI	<.0001	<.0001	<.0001	<.0001

Probability of getting test statistic (F) at least as large as that calculated if null hypothesis is true is shown.
NS=no significant difference between means (alpha=0.05)

Table C3. Dunnett's Test for Comparing Control Mean (Day 0) to Treatment Means

Null hypothesis: Control mean equals treatment mean

ANALYSIS	TREATMENT	STATION James 1	James 2	York 1	York 2
NO2	Day 1	.	**	.	**
	Hold Time	**	**#	**	**
	Day 7-frz	**#	**	**#	**
	Day 28-frz	**	**#	**#	**
NO23	Day 1	.	.	.	**
	Hold Time	.	.	.	m
	Day 7-frz	.	**	.	**
	Day 28-frz	**	.	**	**
NH3	Day 1	.	.	*	.
	Hold Time	.	.	.	m
	Day 7-frz	.	.	.	.
	Day 28-frz	.	.	.	**
TKN	Day 1	*	.	.	.
	Hold Time	**	.	.	.
	Day 7-frz	**	.	.	.
	Day 28-frz	.	.	.	.
OP	Day 1	*#	*#	**#	.
	Hold Time	.	**	.	**
	Day 7-frz	.	*#	.	.
	Day 28-frz	**#	*#	.	**
TDP	Day 1	.	**	.	.
	Hold Time	.	.	.	**
	Day 7-frz	.	.	.	**
	Day 28-frz	.	.	.	**
TP	Day 1	**	**	.	.
	Hold Time	.	**	.	*
	Day 7-frz	**	**	**	.
	Day 28-frz	.	**	**	.
SS	Day 1	*	.	*	**
	Hold Time	.	.	.	.
	Day 7-frz	.	**	**	.
	Day 28-frz	.	.	.	**
SI	Day 1	**	.	.	.
	Hold Time	**	**	**	.
	Day 7-frz	**	**	.	**
	Day 28-frz	**	**	**	**

* = significant difference between means (alpha=0.05)
** = significant difference between means (alpha=0.01)
. = no significant difference between means
m = missing data group
# = difference is not measurable

Table C4. Scheffe's Multiple Contrasts Procedure
Null hypothesis: Mean of Day 0, Day 1, and Hold time means equals freezing treatment mean.

		STATION			
ANALYSIS	TREATMENT	James 1	James 2	York 1	York 2
NO2	Day 7-frz	*#	*#	*#	**
	Day 28-frz	**#	.	.	**#
NO23	Day 7-frz	.	**	.	**
	Day 28-frz	**	.	**	*
NH3	Day 7-frz	.	.	*	.
	Day 28-frz	.	.	*#	**
TKN	Day 7-frz	.	.	.	.
	Day 28-frz	.	.	.	.
OP	Day 7-frz	.	.	.	.
	Day 28-frz	**#	**	.	**
TDP	Day 7-frz	.	.	.	.
	Day 28-frz	.	.	.	**
TP	Day 7-frz	.	**	**	.
	Day 28-frz	.	**	**	.
SS	Day 7-frz	.	.	.	.
	Day 28-frz	.	.	.	.
SI	Day 7-frz	**	**	**	**
	Day 28-frz	**	**	**	**

*=significant difference between means (alpha=0.05)
**=significant difference between means (alpha=0.01)
.=no significant difference between means
#=difference is not measurable

Table C5. Tukey's Multiple Comparisons Procedure
Null hypothesis: Treatment means are equal

		STATION TREATMENT															
		James 1				James 2				York 1				York 2			
ANALYSIS	TREATMENT	D0	D1	HT	D7f	D0	D1	HT	D7f	D0	D1	HT	D7f	D0	D1	HT	D7f
NO2	Day 1	.				*#				.				*			
	Hold Time	*	*			*	*#			*	*			*	*		
	D7-frz	*#	*#	*		*	*#	.		*#	*#	*#		*	*	*	
	D28-frz	*	*#	*	.	*#	.	*	*	*#	*#	*#	.	*	*	*	*#
NO23	Day 1	.				.				.				*			
	Hold Time	.	.			.	.			.	.			m	m		
	D7-frz	.	.	.		*	.	*		.	.	.		*	.	m	
	D28-frz	*	*	*	*	.	.	.	.	*	*	*	.	*	.	m	.
NH3	Day 1	.				.				.				.			
	Hold Time	.	.			.	.			.	*			m	m		
	D7-frz	.	.	.		.	.	.		.	*	.		.	.	m	
	D28-frz	.	.	.	.	.	.	.	.	.	.	.	*	*	*	m	*
OP	Day 1	.				.				*#				.			
	Hold Time	.	.			*	.			.	*#			*	.		
	D7-frz	.	.	.		.	.	.		.	*#	.		.	.	*	
	D28-frz	*#	*#	*#	.	.	*	*	*	.	*#	.	.	*	*	*	*
TKN	Day 1	*				.				.				.			
	Hold Time	*	.			.	.			.	.			.	.		
	D7-frz	*	.	.		.	.	.		.	.	.		.	.	.	
	D28-frz	.	.	*	*	.	.	.	.	.	.	.	.	.	.	.	.
TDP	Day 1	.				*				.				.			
	Hold Time	.	.			.	*			.	.			*	*		
	D7-frz	.	.	.		.	*	.		.	.	.		*	*	*	
	D28-frz	.	.	.	.	.	.	.	.	.	.	.	.	*	*	*	*
TP	Day 1	*				*				.				.			
	Hold Time	.	*			*	.			.	.			.	*		
	D7-frz	*	.	*		*	.	.		*	*	*		.	.	.	
	D28-frz	.	.	.	.	*	*	*	*	*	*	*	*	.	.	*	.
SS	Day 1	*				.				.				*			
	Hold Time	.	.			.	.			.	.			.	.		
	D7-frz	.	.	.		*	.	.		*	.	.		.	.	.	
	D28-frz	.	*	.	.	.	.	.	.	.	.	.	.	*	.	.	.
SI	Day 1	*				.				.				.			
	Hold Time	*	*			*	*			*	*			.	.		
	D7-frz	*	*	*		*	*	*		.	*	.		*	*	*	
	D28-frz	*	*	*	*	*	*	*	*	*	*	.	.	*	*	*	*

*=significant difference between means(alpha=0.05)
.=no significant difference between means
m=missing data group
#=difference is not measurable

Table C6. Kolmogorov-Smirnov Test for Normality
Null Hypothesis: Data are normally distributed.

ANALYSIS	TREATMENT	STATION James 1	James 2	York 1	York 2
NO2	Day 0	---	NS	---	NS
	Day 1	.001	.006	.003	NS
	Hold Time	.003	.003	.016	NS
	Day 7-frz	---	.006	---	.016
	Day 28-frz	.001	---	.016	.001
NO23	Day 0	NS	NS	NS	NS
	Day 1	NS	NS	NS	NS
	Hold Time	NS	NS	NS	m
	Day 7-frz	NS	NS	NS	.048
	Day 28-frz	NS	NS	NS	NS
NH3	Day 0	NS	NS	.037	NS
	Day 1	NS	NS	NS	NS
	Hold Time	NS	NS	NS	m
	Day 7-frz	NS	NS	NS	NS
	Day 28-frz	NS	NS	NS	NS
TKN	(All treatments & stations NS)				
SS	(All treatments & stations NS)				
SI	Day 0	NS	NS	.026	NS
	Day 1	NS	.003	NS	.043
	Hold Time	.045	NS	.048	.003
	Day 7-frz	NS	NS	.007	NS
	Day 28-frz	NS	NS	NS	NS
OP	Day 0	.001	NS	---	.016
	Day 1	.006	.001	.001	.006
	Hold Time	.001	.006	.006	.031
	Day 7-frz	---	.037	.037	.037
	Day 28-frz	NS	.003	---	NS
TDP	Day 0	.008	.025	.042	NS
	Day 1	.005	.016	.013	NS
	Hold Time	.017	.023	.013	NS
	Day 7-frz	NS	.022	.014	NS
	Day 28-frz	NS	NS	NS	NS
TP	Day 0	.048	NS	NS	NS
	Day 1	.015	NS	NS	.015
	Hold Time	NS	NS	.016	NS
	Day 7-frz	NS	.004	NS	NS
	Day 28-frz	.006	NS	NS	NS

Probability of getting test statistic at least as large as that calculated if null hypothesis true is shown.
NS = deviation from non-normality is not significant (alpha=0.05)
--- = data group has no variance
m = missing data group

Table C7. Bartlett's Test for Homogeneity of Variance
Null hypothesis: Variances are equal.

ANALYSIS	STATION James 1	James 2	York 1	York 2
NO2	NS	NS	NS	.009
NO23	<.001	<.001	<.001	<.001
NH3	NS	<.001	<.001	<.001
TKN	.046	NS	.001	<.001
OP	<.001	.003	.011	.001
TDP	<.001	<.001	<.001	NS
TP	<.001	<.001	.015	NS
SS	<.001	.011	.008	NS
SI	.016	.004	.001	.002

Probability of getting test statistic at least as large as that calculated if null hypothesis true is shown.
NS = deviation from homogeneity is not significant(alpha=0.05)

Table C8. Rank means used for nonparametric tests

ANALYSIS	TREATMENT	STATION James 1	James 2	York 1	York 2
NO2	Day 0	53.00	52.81	51.50	46.23
	Day 1	51.04	38.27	47.19	58.77
	Hold Time	7.42	15.27	10.69	7.00
	Day 7-frz	27.50	14.15	23.50	21.85
	Day 28-frz	26.04	44.50	32.12	31.15
NO23	Day 0	32.58	38.27	43.04	40.19
	Day 1	29.81	34.58	41.12	29.42
	Hold time	42.42	45.04	34.92	m
	Day 7-frz	45.31	11.88	28.96	14.31
	Day 28-frz	14.88	32.88	16.96	22.08
NH3	Day 0	34.83	22.65	35.38	34.54
	Day 1	27.69	37.15	14.13	36.08
	Hold time	33.27	35.92	38.88	m
	Day 7-frz	29.08	32.12	45.42	27.88
	Day 28-frz	37.81	37.15	27.27	7.50
TKN	Day 0	8.63	25.69	22.50	18.69
	Day 1	21.94	16.56	15.06	22.75
	Hold time	32.38	24.00	16.50	29.19
	Day 7-frz	27.93	19.88	17.75	9.06
	Day 28-frz	10.13	16.38	30.69	22.81
OP	Day 0	29.88	38.92	38.50	30.04
	Day 1	25.08	25.54	14.38	40.88
	Hold time	29.88	18.15	43.69	54.58
	Day 7-frz	32.00	28.46	29.92	28.42
	Day 28-frz	48.15	53.92	38.50	11.08
TDP	Day 0	32.73	35.31	28.73	29.85
	Day 1	17.69	13.92	26.62	27.00
	Hold time	35.62	50.23	53.31	55.42
	Day 7-frz	45.96	43.15	22.12	45.58
	Day 28-frz	33.00	22.38	34.23	7.15
TP	Day 0	50.88	58.00	26.92	35.58
	Day 1	13.69	26.62	17.65	19.46
	Hold time	49.04	41.19	18.04	52.88
	Day 7-frz	18.50	29.19	57.15	37.31
	Day 28-frz	32.88	10.00	45.23	19.77
SS	Day 0	34.05	37.70	32.60	34.65
	Day 1	11.50	21.90	17.90	17.60
	Hold time	25.20	21.40	34.40	27.85
	Day 7-frz	23.65	17.10	14.10	29.20
	Day 28-frz	31.22	29.40	28.50	14.67
SI	Day 0	46.00	55.08	18.77	19.00
	Day 1	59.00	48.38	20.50	21.77
	Hold time	32.38	34.54	38.81	19.85
	Day 7-frz	20.62	20.00	31.69	59.00
	Day 28-frz	7.00	7.00	55.23	45.38

m = missing data group

Table C9. Kruskal-Wallis Nonparametric
Oneway Analysis of Variance
Null hypothesis: Mean ranks are equal

ANALYSIS	STATION			
	James 1	James 2	York 1	York 2
NO2	<.0001	<.0001	<.0001	<.0001
NO23	.0003	.0001	.0025	.0001
NH3	NS	NS	.0003	<.0001
TKN	<.0001	NS	NS	.0118
OP	.0001	<.0001	.0001	<.0001
TDP	.0025	<.0001	<.0001	<.0001
TP	<.0001	<.0001	<.0001	<.0001
SS	.0037	.0128	.0028	.0069
SI	<.0001	<.0001	<.0001	<.0001

Probability of getting test statistic at least as large as that calculated if null hypothesis true is shown.
NS=No significant difference between mean ranks(alpha=0.05)
Test statistic (chi-squared) is corrected for ties in rank.

Table C10. Dunn's Nonparametric Multiple Comparisons Procedure
Null hypothesis: Mean ranks are equal.

		STATION TREATMENT															
		James 1				James 2				York 1				York 2			
ANALYSIS	TREATMENT	D0	D1	HT	D7f	D0	D1	HT	D7f	D0	D1	HT	D7f	D0	D1	HT	D7f
NO2	Day 1	.				.				.				.			
	Hold Time	*	*			*	*			*	*			*	*		
	D7-frz	*	*	.		*	*	.		*	*	.		*	*	.	
	D28-frz	*	*	.	.	.	.	*	*	.	.	*	.	.	*	*	.
NO23	Day 1	.				.				.				.			
	Hold Time	.	.			.	.			.	.			m	m		
	D7-frz	.	.	.		*	*	*		.	.	.		*	.	m	
	D28-frz	.	.	*	*	.	.	.	*	*	*	.	.	*	.	m	.
NH3	Day 1	.				.				*				.			
	Hold Time	.	.			.	.			.	*			m	m		
	D7-frz	.	.	.		.	.	.		.	*	.		.	.	m	
	D28-frz	.	.	.	.	.	.	.	.	.	.	.	.	*	*	m	*
OP	Day 1	.				.				*				.			
	Hold Time	.	.			.	.			.	*			*	.		
	D7-frz	.	.	.		.	.	.		.	.	.		.	.	*	
	D28-frz	.	*	.	.	.	*	*	*	.	*	.	.	.	*	*	.
TKN	Day 1	.				.				.				.			
	Hold Time	*	.			.	.			.	.			.	.		
	D7-frz	*	.	.		.	.	.		.	.	.		.	.	*	
	D28-frz	.	.	*	*	.	.	.	.	.	.	.	.	.	.	.	.
TDP	Day 1	.				*				.				.			
	Hold Time	.	.			.	*			*	*			*	*		
	D7-frz	.	*	.		.	*	.		.	.	*		.	.	.	
	D28-frz	.	.	.	.	.	.	*	.	.	.	.	.	*	.	*	*
TP	Day 1	*				*				.				.			
	Hold Time	.	*			.	.			.	.			.	*		
	D7-frz	*	.	*		*	.	.		*	*	*		.	.	.	
	D28-frz	.	.	.	.	*	.	*	.	.	*	*	.	.	.	*	.
SS	Day 1	*				.				.				.			
	Hold Time	.	.			.	.			.	.			.	.		
	D7-frz	.	.	.		*	.	.		*	.	*		.	.	.	
	D28-frz	.	*	.	.	.	.	.	.	.	.	.	.	*	.	.	.
SI	Day 1	.				.				.				.			
	Hold Time	.	*			.	.			.	.			.	.		
	D7-frz	*	*	.		*	*	.		.	.	.		*	*	*	
	D28-frz	*	*	*	.	*	*	*	.	*	*	.	*	*	*	*	.

*=significant difference between mean ranks(alpha=0.05)
.=no significant difference between mean ranks
m=missing data group

APPENDIX D
LABORATORY METHODS

Analysis:	**Ammonia, dissolved**
Storet number:	00608
References:	1. U.S. EPA (1979) Methods for Chemical Analysis of Water and Wastes, Method 350.1. 2. Standard Methods for the Examination of Water and Wastewater (1975) 14th Edition, p. 616, Method 604.
Brief:	An automated phenate method. Alkaline Phenol and hyp-chlorite react with ammonia to form indophenol blue which is intensified with sodium nitroprusside and measured colorimetrically.
Modification:	None

Analysis:	**Nitrate-Nitrite, dissolved**
Storet number:	00631
References:	1. U.S. EPA (1979) Methods for Chemical Analysis of Water and Wastes, Method 353.2. 2. Standard Methods for the Examination of Water and Wastewater (1975) 14th Edition, pp. 620-624, Method 605. 3. Strickland and Parsons (1972) A Practical Handbook of Seawater Analysis, pp. 127-130. 4. Technicon Industrial Method No. 100-70W (1973) Nitrate and Nitrite in Water and Wastewater.
Brief:	An automated method where nitrate is reduced to nitrite by a copper-cadmium column, and determined by diazotization with sulfamilamide and coupling with N-(1-naphtyl)-ethylenediamine dihydrochloride to form an azo dye which is measured colorimetrically.
Modification:	None

Analysis:	**Total Kjeldahl Nitrogen**
Storet number:	00625
References:	1. U.S. EPA (1979) Methods for Chemical Analysis of Water and Wastes, Method 351.3, Method 350.1. 2. Standard Methods for the Examination of Water and Wastewater (1975) 14th Edition, p. 437, Method 421.
Brief:	The sample is digested using heat, conc. sulfuric acid, mercuric sulfate (catalyst). The residue is diluted and made alkaline with a hydroxide thiosulfate solution. The ammonia is distilled into boric acid solution and read by automated phenate colorimetry.
Modification:	Use of automated phenate procedure to read resulting ammonia.

Analysis:	**Total Phosphorus**
Storet number:	00665
References:	1. U.S. EPA. (1979) Methods for Chemical Analysis of Water and Wastes, Method 365.2. 2. Standard Methods for the Examination of Water and Wastewater (1975) 14th Edition, p. 476, pp. 481-482, Method 425C.111, Method 425E.
Brief:	An acid persulfate digestion, with the liberated orthophosphate determined by single reagent, blue-colored complex ascorbic acid reduction and measured colorimetrically.
Modification:	None

Analysis:	**Residue, Total non-filterable**
Storet number:	00530
References:	1. U.S. EPA (1979) Methods for Chemical Analysis of Water and Wastes, Method 160.2. 2. Standard Methods for the Examination of Water and Wastewater (1975) 14th Edition, p. 94, Method 208D.
Brief:	A mixed sample is filtered through a glass fiber filter and filter is dried to constant weight at 103-105 degrees C.
Modification:	None

Analysis:	**Silicates, dissolved**
Storet number:	None
References:	1. Technicon Industrial Method No. 186-72W (1973) "Silicates in Water and Seawater". 2. Strickland and Parsons, A Practical Handbook of Seawater Analysis (1972) pp. 139-140.
Brief:	An automated procedure based on the reduction of a silicomolybdate in acidic solution to molybdenum by blue ascorbic acid. Oxalic acid eliminates interference from phosphates.
Modification:	None

Analysis:	**Nitrite, dissolved**
Storet number:	00630
References:	1. U.S. EPA. (1979) Methods for Chemical Analysis of Water and Wastes Method 353.2. 2. Standard Methods for the Examination of Water and Wastewater (1975) 14th Edition, pp. 620-624, Method 605. 3. Strickland and Parsons (1972) A Practical Handbook of Seawater Analysis, pp. 127-130.
Brief:	An automated method where nitrite is determined by diazotizing with Sulfanilamide and coupling with N-(1-naphthyl)-ethylenediamine dihydrochloride to form an azo dye which is measured colorimetrically.
Modification:	None

Analysis:	**Orthophosphate**
Storet number:	00671
References:	1. U.S. EPA (1979) Methods for Chemical Analysis of Water and Wastes, Method 365.2. 2. Standard Method for the Examination of Water and Wastewater (1975) 14th Edition, pp. 481-482.
Brief:	Orthophosphate is determined by single reagent reaction of antimony phospho-molybdate complex reduced to a blue-colored complex by ascorbic acid and measured colorimetrically.
Modification:	None